

COKE FORMATION DURING NAPHTHA PYROLYSIS

A Thesis Submitted
in Partial Fulfilment of the Requirements
for the Degree of

MASTER OF TECHNOLOGY

by

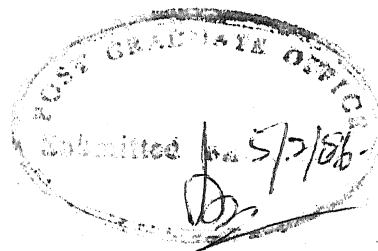
DURJYOGHARAN SAHU

to the

DEPARTMENT OF CHEMICAL ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY, KANPUR

FEBRUARY, 1986

(11)



CERTIFICATE

This is to certify that the present work entitled
"COKE FORMATION DURING NAPHTHA PYROLYSIS" by Shri Durjyogharan
Sahu has been carried out under my supervision and has not
been submitted elsewhere for a degree.

February 4 , 1986

Dr. D. Kunzru

Dr. D. Kunzru
Professor
Department of Chemical Engineering
Indian Institute of Technology
Kanpur-208016, INDIA

CHE-1886-M-SAH-COK

107 86

CENTRAL LIBRARY

no. A 91916

Thesis
665.772
Sa19c

ACKNOWLEDGEMENTS

I express my sincere gratitude to Professor D. Kunzru for his inspiring guidance, valuable advice and meticulous attention in each and every step of this investigation.

I am grateful to Mr. P. V. Rao for his assistance throughout this investigation.

I am very much thankful to Mr. A. Sen, Mr. D. Bandopadhyay for inspiring me all the time.

I shall be failing in my duty if I don't mention the names of my friends and colleagues specially, Mr. S. K. Sengupta, Mr. U. Manna, Mr. D. Sanyal, Mr. T. K. Poddar, Mr. D. R. Giri, Mr. P. K. Maji, Mr. R. Haldar, Mr. M. Ghosh, Mr. J. Srinivasa Rao, Mr. G. Gangadhar who helped me in various ways. Thanks are also due to Mr. K. K. Ghosh.

Special thanks are extended to Mr. N. K. Metia for helping me throughout the experiment.

I also take this opportunity to thank all the staff members of the department for providing necessary help from time to time.

Finally, I must thank Mr. B. S. Pandey for efficient typing and Mr. A. K. Ganguly for drawings.

Durjyogharan Sahu
Author

CONTENTS

List of Figures	vi
List of Tables	viii
Nomenclature	ix
Abstract	x

CHAPTER

1	INTRODUCTION	1
2	LITERATURE REVIEW	4
3	EXPERIMENTAL APPARATUS AND PROCEDURE	9
	3.1 Experimental Apparatus	9
	3.2 Experimental Procedure	11
	3.3 Liquid Analysis	13
	3.4 Gas Analysis	14
4	RESULT AND DISCUSSION	16
	4.1 Effect of Material of Construction	16
	4.1.1 Product Distribution	20
	4.2 Effect of Decoking	20
	4.3 Effect of Aromatic Concentration	23
	4.4 Effect of Process Variables	24
	4.5 Effect of Thiophene Content of Feed	26
	4.6 Modelling of Coke Formation	38
	4.6.1 Modelling of Coke Formation During Pyrolysis of Thiophene- free-Naphtha	38
	4.6.2 Modelling of Coke Formation During Pyrolysis of Thiophene Containing Naphtha	48

CHAPTER

5	CONCLUSIONS AND RECOMMENDATIONS	50
	5.1 Conclusions	50
	5.2 Recommendations	51
	REFERENCES	52

APPENDIX

A	Calibration Details of Various Columns	56
B	Rates of Coke Formation with Run Time at Different Temperatures and Space Time	57
C	Computer Program for the Non-linear Least Square Estimation of Model Parameters	61

LIST OF FIGURES

FIGURE	TITLE	Page
1	Schematic Diagram of the Experimental Set-up	10
2	Effect of Material of Construction on the Rate of Coke Formation ($T = 1083 \text{ K}$; $\delta = 0.47$; $\tau = 0.49\text{s}$)	18
3	Effect of Decoking on the Rate of Formation of Coke on InConel 600 Surface ($T = 1083 \text{ K}$; $\delta = 0.47$; $\tau = 0.49\text{s}$)	22
4	Effect of Inlet Benzene Concentration on the Rate of Coke Deposition on InConel 600 surface ($T = 1083 \text{ K}$; $\delta = 0.47$; $\tau = 0.49\text{s}$)	25
5	Effect of Temperature on Asymptotic Rate of Coking on InConel 600 Surface ($\delta = 0.47$)	27
6	Effect of Inlet Partial Pressure of Naphtha on Asymptotic Rate of Coking on Inconel 600 Surface ($T = 1083 \text{ K}$)	28
7	Effect of Thiophene on Rate of Coke Formation on Inconel 600 Surface ($T = 1083 \text{ K}$; $\delta = 0.47$; $\tau = 0.49\text{s}$)	30
8	Variation of Asymptotic Coking Rate with Thiophene Concentration of Feed	31
9	Effect of Thiophene Concentration in Naphtha on Gas and Liquid Yields	32
10	Determination of Reaction Order for Rate of Coking at Different Temperatures	40
11	Determination of Rate Constant for Asymptotic Rate of Coking at Different Temperatures	42

12	Arrhenius Plot for the Deposition of Coke	43
13	Comparison Between Calculated and Experimental Asymptotic Rate of Coking	47
14	Effect of Inlet Thiophene Concentration on Reaction Order for Rate of Coke Formation	49

LIST OF TABLES

TABLE	TITLE	Page
1	Details of Chromatographic Conditions	15
2	Characteristic of the Naphtha Feed	17
3	Product Yields During Naphtha Pyrolysis	21
4	Product Distribution During Pyrolysis of Naphtha Containing Thiophene	34
5	Effect of Process Variables on the Rate of Coking of Thiophene-Free-Naphtha	44
6	Parameter Estimates for the Non-linear Coking Model	46

NOMENCLATURE

k_o, k'_o	frequency factor
C_A	concentration of aromatics, $\frac{\text{Kg mole}}{\text{m}^3}$
E	activation energy, $\frac{\text{Kcal}}{\text{mole}}$
n	reaction order with respect to coke
r_a	asymptotic rate of coking, $\text{Kg/m}^2 \text{ hr}$
T	temperature, K
T_m	average temperature, K
R	gas constant, $\frac{\text{Kcal}}{\text{K-mole K}}$

Greek Symbols

δ	weight ratio of steam to naphtha
τ	space time, s

ABSTRACT

Rates of coke formation during naphtha pyrolysis have been investigated in a jet-stirred reactor both for thiophene-free naphtha and thiophene containing naphtha on Inconel 600 surfaces at atmospheric pressure in the temperature range of 1073-1103 K. The effect of temperature, space time, weight ratio of steam to naphtha, aromatic and thiophene content of feed and material of construction on the rates of coke deposition was measured by periodically weighing a small metalplate suspended into the centre of the reactor.

Coking rates increased as the temperature, space time and aromatic content of the feed was increased whereas it decreased with an increase in the weight ratio of steam to naphtha and the thiophene content of the feed. Addition of thiophene significantly reduced the aromatic yields. Rate of coke formation could be modelled using a power law form.

CHAPTER 1

INTRODUCTION

Pyrolysis of hydrocarbons, such as naphtha, ethane and propane is of great importance for the production of olefins such as ethylene, propylene and butadiene which are the building blocks of the petrochemical industry. The preferred feedstock varies from country to country. In the U.S., it is mainly a mixture of ethane and propane, whereas in Japan, Europe and India, the preferred feedstock is naphtha. Naphtha is a complex mixture of hydrocarbons and is normally characterised with respect to its specific gravity, carbon to hydrogen ratio, ASTM boiling range and PONA analysis, which provides the distribution of paraffins, olefins, naphthenes and aromatics. A major problem associated with any hydrocarbon pyrolysis is the undesirable formation of coke which deposits on the walls of the pyrolysis coil. Coke is a complex mixture of carbon and hydrogen and can be formed either from the reactants and/or products. The deposition of coke with time gradually increases the pressure drop across the tubular reactor and also reduces the overall heat transfer coefficient across the tube wall due to the extra thermal resistance of the deposited coke layer. Hence, the thicker the coke layer, the higher the tube wall temperature which must be applied to achieve the same fluid temperature and degree of feedstock conversion.

The reactor has to be shut down when the tube wall temperature reaches the limiting value. Depending upon the feedstock and operating conditions, the run lengths are generally limited from 40 to 60 days. The reactor is then decoked by burning with a steam-air mixture. Frequent decoking operation results in loss of production, affect the coil life and utility costs are increased. Coke is also corrosive and can cause metallurgical failure of a reactor.

To design and optimise naphtha crackers, reliable models for the main naphtha pyrolysis as well as models for the coking kinetics during pyrolysis are necessary. Not much information is available on modelling of naphtha pyrolysis or coking kinetics. Quantitative models are not available, but only the qualitative effect of various operating variables is known.

During the last few years, investigations have been made on coke formation during the pyrolysis of various hydrocarbons such as ethane (Albright and McConnell, 1978; Sundaram et al., 1981), propane (Sundaram and Froment, 1979; Trimm and Turner, 1981a), n-hexane (Pramanik and Kunzru, 1985), n-octane (Shah et al., 1976) and naphtha (Newsome and Leftin, 1979; Kumar and Kunzru, 1985). These studies have shown that coke deposition depends on several factors, such as, the aromatic and sulphur content of the feedstock, hydrocarbon partial pressure, temperature, conversion and the material of construction of the reactor.

In an earlier study, (Kumar and Kunzru, 1985), coke deposition in naphtha pyrolysis was studied in a jet stirred reactor and the rate of coke formation was modelled by an approximately second order reaction involving the aromatics. However, the model was not checked either for different aromatic concentrations of the feedstock or for different materials of construction of the reactor. Moreover, the effect of sulfur content of the feed on the rate of coke formation was not investigated. It has been observed that the continuous dosage of sulfur containing compounds such as thiophene, together with heptane feed, influences both the rate of pyrolysis as well as the rate of coking (Bajus et al., 1981). However, it is not clear whether the sulfur caused passivation of the reactor walls or it affected the coke precursors in the gas phase.

The objective of this study was to investigate the effect of the material of construction of the reactor and the aromatic and sulfur content of the feed stock on the rates of coke formation during naphtha pyrolysis. In addition, the effect of temperature, inlet hydrocarbon partial pressure and space time on the rate of coke formation was investigated. A further objective was to model the coking kinetics during naphtha pyrolysis.

CHAPTER 2

LITERATURE REVIEW

Product distribution in the pyrolysis of various hydrocarbons including naphtha is well established and considerable data is available, but very meagre data is available on the rates of coke formation during the pyrolysis of naphtha or even other pure hydrocarbons.

Various investigators have studied the pyrolysis of methane (Eisenberg and Bliss, 1967), ethane (Silcocks, 1956; Snow et al., 1959), propane (Volkan and April, 1977), n-butane (Steacia and Puddington, 1938; Sandler and Chung, 1961), n-hexane (Frey and Hepp, 1933; Ebert et al., 1983), n-heptane (Bajus and Vesely, 1979), n-nonane (Kunzru et al., 1972), 2-pentene (Kunzru et al., 1973), naphtha (Van Damme et al., 1981; Kumar and Kunzru, 1985) and have reported the kinetics and product distribution.

Data on coke formation during pyrolysis is very limited. Hirt and Palmer (1967) studied the coke formation from methane pyrolysis between 1163 and 1373 K and obtained an activation energy of 432 MJ/kmol. Johnson and Anderson (1972) studied the coke formation from acetylene at temperature ranging from 773 to 1273 K and observed both coke and polymer as the products. They suggested that coke and polymer were formed by two competing parallel reactions in the gas phase. Albright

and McConnell (1978) investigated the rate of coke formation in ethane pyrolysis and found that the coking phenomena was significantly affected by the material of construction of the pyrolysis tube and also on the pretreatment given to the reactor. An activation energy of coke formation of 250 to 290 MJ/kmol was reported.

Kinney and Del Bel (1954) studied the pyrolysis of unsaturated aromatic hydrocarbons and suggested that coke is formed from a stepwise condensation of the aromatic rings. Similarly, Virk et al. (1974) have proposed that coke formation occurs from aromatic compounds, mainly from benzene. Shah et al. (1976) studied the coke formation in the thermal cracking of n-octane between 1023 to 1073 K. The coking rate was high during the initial stages of the experiment and then reduced to an asymptotic value. They also observed that the amount of coke formed increased with an increase in the surface to volume ratio of the reactor. Further air (or oxygen) treatment activate the reactor surface to induce more coking whereas H_2S treatment passified it. The reduction in coke formation during hydrocarbon pyrolysis by adding sulfur compounds to the feed is well documented (Bajus et al., 1981). Newsome and Leftin (1979) investigated the rates of coke formation in naphtha pyrolysis in an annular tubular reactor. The coking rates were found to depend on the run time, inlet steam and hydrocarbon partial pressure and temperature. The specific rate of coking was independent of the surface-to-volume ratio of the reactor.

All the above mentioned studies were conducted in tubular flow reactors and the total coke formed measured by either weighing the reactor before and after the experiment or by burning the coke and measuring the effluent gaseous amounts. Since coke is not deposited uniformly along the reactor (Froment and Bischoff, 1961), this result is only average coking rate and precludes a kinetic analysis. To overcome this problem, Sundaram and Froment (1979) developed a jet-stirred completely mixed reactor which allowed the kinetics of the main pyrolysis reaction and kinetics of coking to be determined simultaneously. They measured the amount of coke deposition continuously, by suspending a small cylinder of the same material as the reactor, into the reactor from an electrobalance. For propane pyrolysis, the coking rates were best represented by a model which assumed that coke was formed from propylene by a first order reaction, whereas the coke formation in ethane pyrolysis was modelled as a first order reaction from the C_4+ hydrocarbons (Sundaram et al., 1981). Trimm and Turner (1981a) also studied the coke formation in propane pyrolysis in a jet-stirred reactor and found that once the reactor surface was covered with carbon, the rate of coke deposition was independent of the nature of the surface at all temperatures. Pramanik and Kunzru (1985) investigated the pyrolysis of n-hexane and kinetics of coking in a jet-stirred reactor in the temperature

range of 993-1083 K. The experimental coking rates could be adequately fitted by a model in which ethylene was the coke forming species. Kumar and Kunzru (1985) also used a jet-stirred reactor to study the coke deposition during naphtha pyrolysis and the rate of coke formation was modelled by an approximately second order reaction involving the aromatics.

The reactor surface significantly affects the coke formation during pyrolysis of hydrocarbons. Various investigators have shown that metals present in the reactor surface activate the coke formation. The presence of metals in coke during ethylene cracking has been reported by Albright and coworkers (1978), who have demonstrated that such metals can catalyze the formation of additional coke. Research of Albright and co-workers (1979) on the pyrolysis of hydrocarbons over Incoloy 800 surfaces shows iron to be the predominant metal in the coke.

Since it is well established that the walls of the reactor catalyze the coke formation, most of the methods used to inhibit the coking use some means to passivate the reactor walls. Presulfiding the reactor has been reported to reduce coke formation during the pyrolysis of ethane (Albright and McConnel, 1978), propane (Trimm and Turner, 1981b) and octane (Shah et al., 1976). Bajus et al. (1981; 1983) studied the effect of thiophene, dibenzyl sulfide and dibenzyl disulfide on reaction kinetics and coking of steam cracking of heptane in stainless

steel tubular reactors with relatively large surface areas. The deposition of coke was inhibited considerably due to the formation of metal sulfide which passivated the reactor surface. Bajus et al. (1980) studied the effect of sulfur compounds on straight run naphtha and proposed that during the cracking, intermediate $\text{HS}\cdot$ radicals could be formed from sulfur compounds, such as mercaptans. These radicals might be partly converted to hydrogen sulfide by reaction with hydrocarbons and could also react with the reactor walls to form metal sulfides. This sulfide film inhibits the secondary reaction which leads to the formation of coke. Depeyre et al. (1985) studied the influence of sulfur compounds on n-nonane in a quartz reactor and found that the addition of sulfur compounds to n-nonane steam cracking catalyses the rate of n-nonane decomposition and inhibits secondary reactions leading to the formation of C_2H_4 , C_4H_6 and aromatic compounds. Yields of these secondary products decreased as the weight percentage of sulfur compounds in the feed was increased and sulfur also altered the rate of formation of coke.

From the above literature survey, it is clear that not much information is available for the rate of coke formation in naphtha pyrolysis and very few quantitative models have been published. Moreover, the effect of sulfur compounds on the rate of coke formation during steam cracking of naphtha is not well established.

CHAPTER 3

EXPERIMENTAL APPARATUS AND PROCEDURE

3.1 Experimental Apparatus:

The experiments were conducted in a jet-stirred reactor. A schematic diagram of the equipment is shown in Fig. 1. Liquid naphtha and water from separate graduated burettes were pumped by a double acting reciprocating pump which could be adjusted for flow rates in the range of 0.2 to 30 cc/min. Steam, which was used as an inert was generated in a vaporiser (1.5 Kw) and mixed with naphtha. The mixture of hydrocarbon and steam was passed through another preheater (1.5 Kw) where the mixture was heated to approximately 773 K. The heated mixture was then led into the reactor which was just above the reactor. The product gases from the reactor exited through a central outlet tube which extended above the preheater and was constructed from 25 mm O.D. SS 316 tubing.

The preheater reactor assembly was such that good mixing could be achieved in the reactor. It was made from a 25 mm I.D. SS 316 tubing and the reactor length and volume was 2.3 cm and 11.2 cm³ respectively. The wall separating the reactor and preheater contained thirty two one mm holes, distributed uniformly, which acted as nozzles and ensured good mixing inside the reactor. To provide uniform distribution of the inlet mixture into the reactor, the preheater was packed with

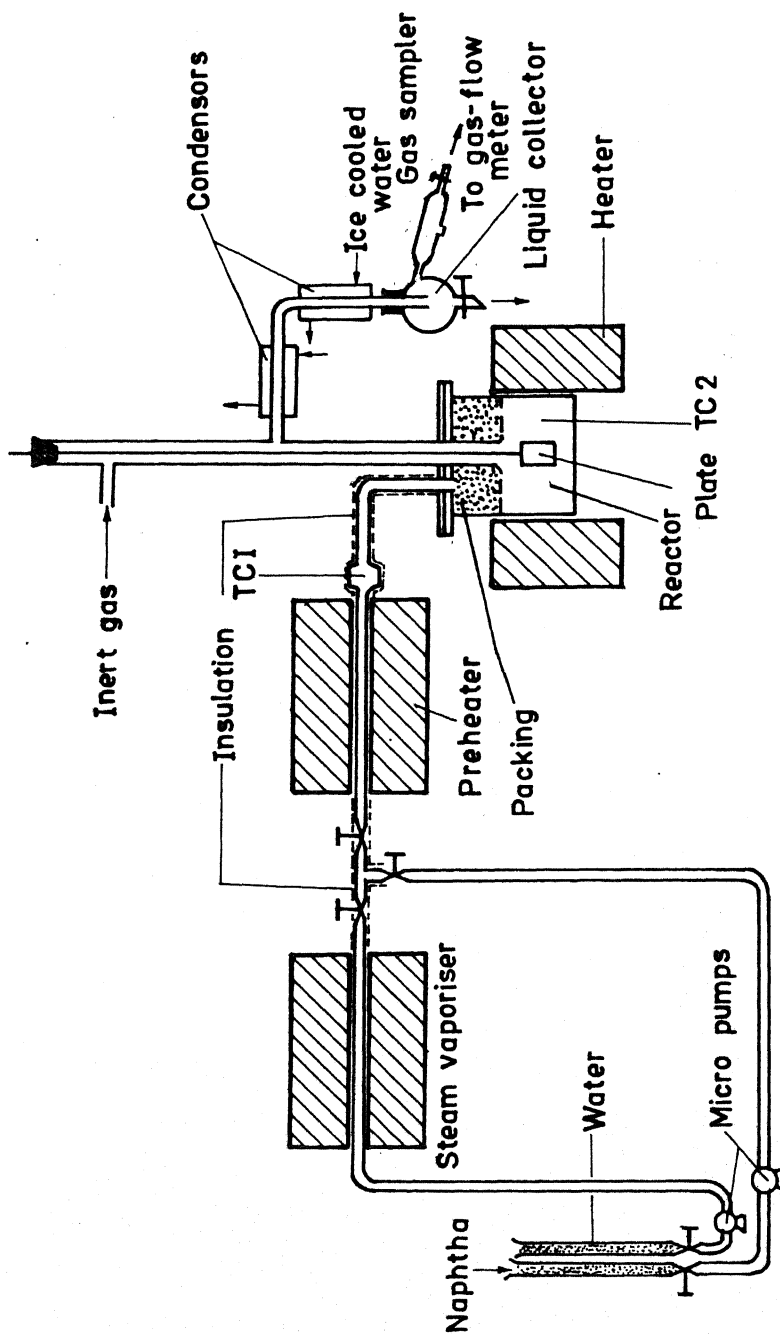


Fig.1 Schematic diagram of the experimental setup

crushed ceramic beads. The preheater-reactor assembly was heated in a controlled electric furnace. The temperature of the reactor was measured and controlled by a temperature indicator-controller (Model CT 806, Century Instrument) which was connected to a chromel-alumel thermocouple placed in a thermowell which extended into the centre of the reactor. The reactor temperature could be controlled to within $\pm 2^{\circ}\text{C}$ of the set value. There was a large temperature gradient in the preheater zone, but, in all the runs, the axial temperature gradient in the main reactor was negligible.

In this set up, both the deposition of coke and product distribution could be measured. For the measurement of coke, a small rectangular metal plate was suspended by means of a wire into the central portion of the reactor through the central outlet tube. The plate was weighed on an electro-balance and resuspended at the centre of the reactor. This was done at periodic intervals during the course of a run. To prevent reaction products from entering the outlet tube, a small flow of nitrogen was passed from the top through the side exit of the outlet tube. The reaction mixture was quenched by passing through two ice-water cooled condensers placed in series. The liquid product was collected and the non-condensables passed through a sampling valve and vented.

3.2 Experimental Procedure:

A run was initiated by first heating the reactor to a temperature $10\text{--}15^{\circ}\text{C}$ higher than the desired temperature.

After the temperature had stabilised, nitrogen gas was passed from the top. The reactor was then flushed with steam for 45 minutes to ensure an inert atmosphere in the set-up. The water flow rate was then fixed to the desired value and naphtha feed started. Since pyrolysis is endothermic, the reactor temperature dropped by 10-15°C once the reaction commenced. Depending upon whether the product distribution or coke deposition was being measured, the procedure was modified.

For measuring the coke deposition, after the temperature had restabilised at the new value, a small plate was suspended by means of a wire into the central portion of the reactor through the central outlet tube. The suspended plate was removed from the reactor at thirty minute intervals, weighed on an electrobalance and resuspended. The accuracy of the balance was 0.01 mg. To prevent any oxidation of the deposited coke, the **plate** was pulled up slowly through the outlet tube so that it cooled to 473-523 K in the relatively cooler portion of the outlet tube. A run was continued till the rate of coke formation became constant. The total duration of the run varied from 2-3 hours. Attempts to measure the coke deposition by suspending the plate directly from an electrobalance were unsuccessful because of vibrational problems during the passage of reactants and products. During a run, the total flow rate of the non-condensables was measured.

At the completion of the run, liquid products were collected and the volume and density measured. The aromatic content of the liquid products was determined by gas chromatographic analysis. Subsequently, the reactor was flushed with steam and the deposited coke on the plate and reactor was burned by passing heated air through the reactor for approximately 30 minutes. The plates were used for the next run after removing the metal oxides by immersing the plate in a solution of acids ($3\% \text{H}_2\text{SO}_4 + 3\% \text{HCl}$) and then cleaning with emery paper.

For measuring the product distribution, no plate was suspended and the top outlet tube was closed with a cork. The total gas and liquid flow rate was measured and the gas from the sampling valve analyzed on a gas chromatograph. The analysis of the liquid products was done as mentioned above.

3.3 Liquid Analysis:

Due to the complexity of the liquid products and the nonavailability of a suitable capillary column, detailed analysis of the liquid fraction was not possible. The aromatic content of the liquid product was determined on a 3 mm I.D., 3 m long DEGS (diethylene glycol succinate) column. The calibration data for liquid analysis is shown in Appendix A. Details of the chromatographic conditions are given in Table 1.

3.4 Gas Analysis:

The gaseous products formed in the pyrolysis were analysed on gas chromatograph using a thermal conductivity detector. A 3mm I.D., 3 m long Duropak column operated at 42°C was used to analyse the C₃ and C₄ gases. Hydrogen, methane, ethane and ethylene could not be completely separated on this column and were analysed on a 3 mm I.D., 2 m long poropak Q column also operated at 42°C. The calibration data for the gas analysis on the different columns is shown in Appendix A. Details of the chromatographic conditions are given in Table 1.

Table 1: Details of the Chromatographic Condition

Column packing	Column size	Oven temp., K	Detector temp., K	Injector temp., K	Flow rate of N ₂ , m ³ /s x 10 ⁶	Filament current (mA)	Components separated
Duopak	3 mm I.D. x 3 m	315.0	343.0	343.0	0.2833	90	C ₃ H ₆ , C ₄ H ₁₀
Poropak, Q	3 mm I.D. x 3 m	315.0	343.0	343.0	0.5666	90	H ₂ , CH ₄ , C ₂ H ₆ , C ₂ H ₄
25% DEGS on Chromosorb P	3 mm I.D. x 3 m	363.0	413.0	413.0	0.6667	90	Benzene, Toluene, Xylene

CHAPTER 4

RESULTS AND DISCUSSION

To study the coke formation during naphtha pyrolysis, experiments were conducted at atmospheric pressure in the temperature range 1073 to 1103 K. The naphtha was obtained from Bharat Refineries, Bombay, which processes Arabian crude and the feed characteristics are given in Table 2. Steam was used as an inert diluent and the weight ratio of steam to naphtha, δ , was varied from 0.47 to 0.7 and the space time from 0.2 to 0.49 seconds. The effect of aromatic and sulfur concentration of naphtha feed on the rate of coking was studied by adding benzene or thiophene to the naphtha feed. The benzene concentration was varied from 8.1 to 21.07 mole % and the thiophene content from 0 to 1.2 wt.%. The rate of coking was investigated on three metal surfaces viz. SS 304, SS 316 and Inconel 600. For all the runs, a material balance was made and the water balance was 98-99% and the hydrocarbon balance was 96 - 98%.

4.1 Effect of Material of Construction:

The effect of material of construction was investigated on SS 304, SS 316 and Inconel 600. For all the runs, the temperature, δ and space time, τ , were maintained at 1083 K, 0.47 and 0.49 s, respectively. The variation in the rate of coke formation with run time is shown in Fig. 2. For all the

Table 2: Characteristics of the Naphtha Feed

Properties:

(i)	Density (298 K)	0.701 gm/ml
(ii)	ASTM Distillation	°C
	IBP	47
	5%	59
	10%	63
	50%	87
	90%	119
	95%	129
	FBP	156
(iii)	PONA	wt. %
	Normal paraffins	33.7
	Total paraffins	73.6
	Naphthenes	17.4
	Benzene + Toluene + Xylene	8.5
(iv)	Total sulfur	0.05
	Average molecular weight	91

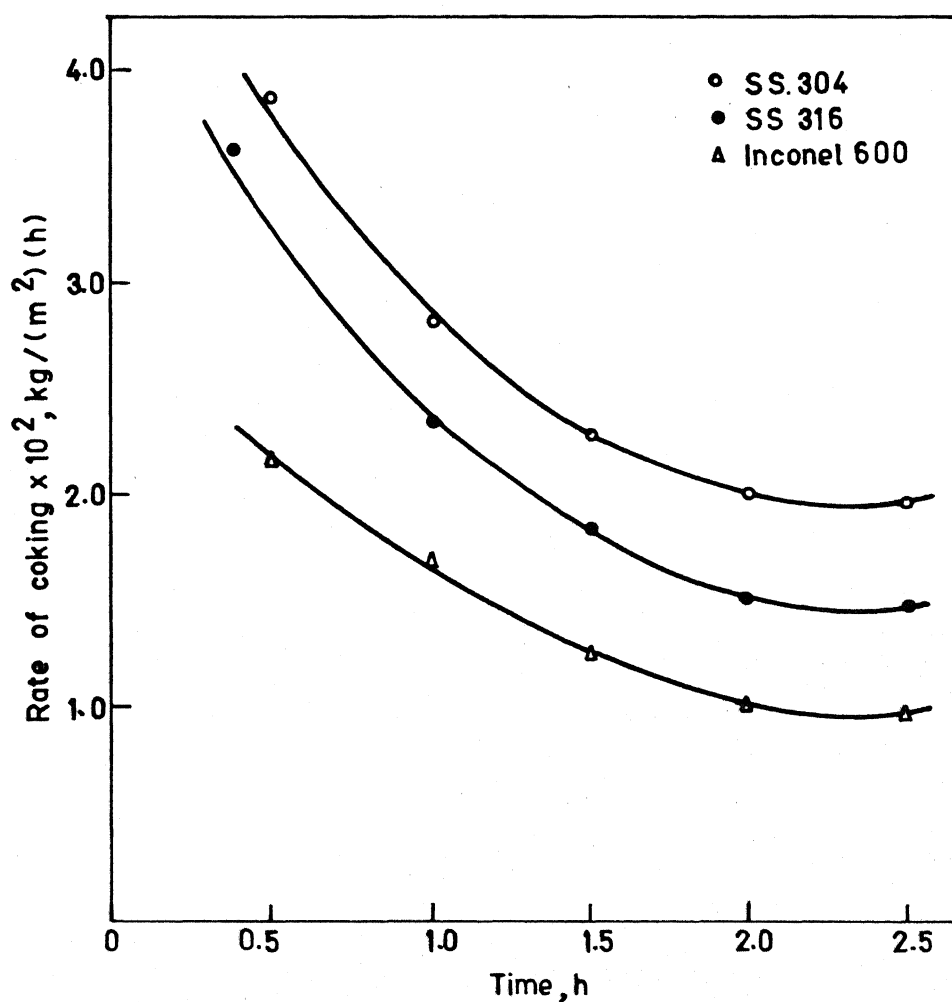


Fig. 2 Effect of material of construction on the rate of coke formation ($T = 1083\text{K}$, $\delta = 0.47$, $\tau = 0.49\text{s}$)

runs, rates of coke deposition are initially high and then decrease to a constant value with progress of the reaction. A plausible explanation for this variation is that initially the bare metal surface catalyzes the coke formation and as the coke gradually deposits on the surface, the metal catalytic activity is progressively reduced. The asymptotic coking rate period, then, corresponds to coke deposition on the metal surface completely covered with coke. Similar trends for rates of coke formation have been reported during the pyrolysis of n-octane (Shah et al., 1976), naphtha (Kumar and Kunzru, 1985), propane (Trimm and Turner, 1981a) and n-hexane (Pramanik and Kunzru, 1985). As shown in this figure, the coking rates were highest on SS 304 and lowest on Inconel 600. This indicates that coking rate is dependent on the material of construction of the reactor. Mandal (1984) also reported coking rates during n-hexane pyrolysis to be lower on Inconel 600 than on SS 304. The dependency of coking rates on the nature of the metal surface has also been reported by Brown and Albright (1976), Albright and McConnel (1979). Contrary to these findings Trimm and Turner (1981a) reported that although the initial coking rates were different, the asymptotic coking rates were identical for different surfaces. Since, in this study, the coking rates were significantly lower on Inconel 600, subsequent investigations were done only on Inconel 600 surface.

4.1.1 Product Distribution

For some runs on Inconel 600, the major gaseous products were also determined. As expected, the major products were ethylene, propylene, methane, together with small amounts of hydrogen, butane and ethane. The aromatics constituted a major portion of the organic liquid products. The product distribution at 1083 K and a space time of 0.49 s is shown in Table 3. These yields compare favourably with those reported in the literature (Kumar and Kunzru, 1985). To check the reproducibility of the product distribution and coke deposition measurements, an identical run was repeated three times. The rates of coking were reproducible to within $\pm 1\%$ and the product distribution to within $\pm 2\%$.

4.2 Effect of Decoking:

To study the effect of metal oxides formed during decoking on the rate of coke formation, an identical run was made first on an Inconel surface from which the oxides had been removed by treating with 3% H_2SO_4 + 3% HCl solution and then with the oxide layer formed during decoking still present. The variation of the rate of coke formation with run time for the two cases is shown in Fig. 3. As shown in this figure, the presence of metal oxides increases the rate of coke formation. The effect of the metal oxide was reproducible as checked by again measuring the rate of coke formation on the decoked (but not cleaned) surface. Since the rates were identical, these points have not been shown in Fig. 3.

Table 3: Product Yields During Naphtha Pyrolysis

Temperature = 1083 K;

$\delta = 0.47$ Kg steam/Kg naphtha

$\tau = 0.49$ s

<u>Component</u>	<u>Yield, Wt.% of feed</u>
hydrogen	1.20
methane	15.92
ethylene	25.32
ethane	2.36
propylene	7.32
n-butane	0.05
other gases	28.83
Benzene + Toluene + Xylene	14.7
higher boiling liquid	2.85

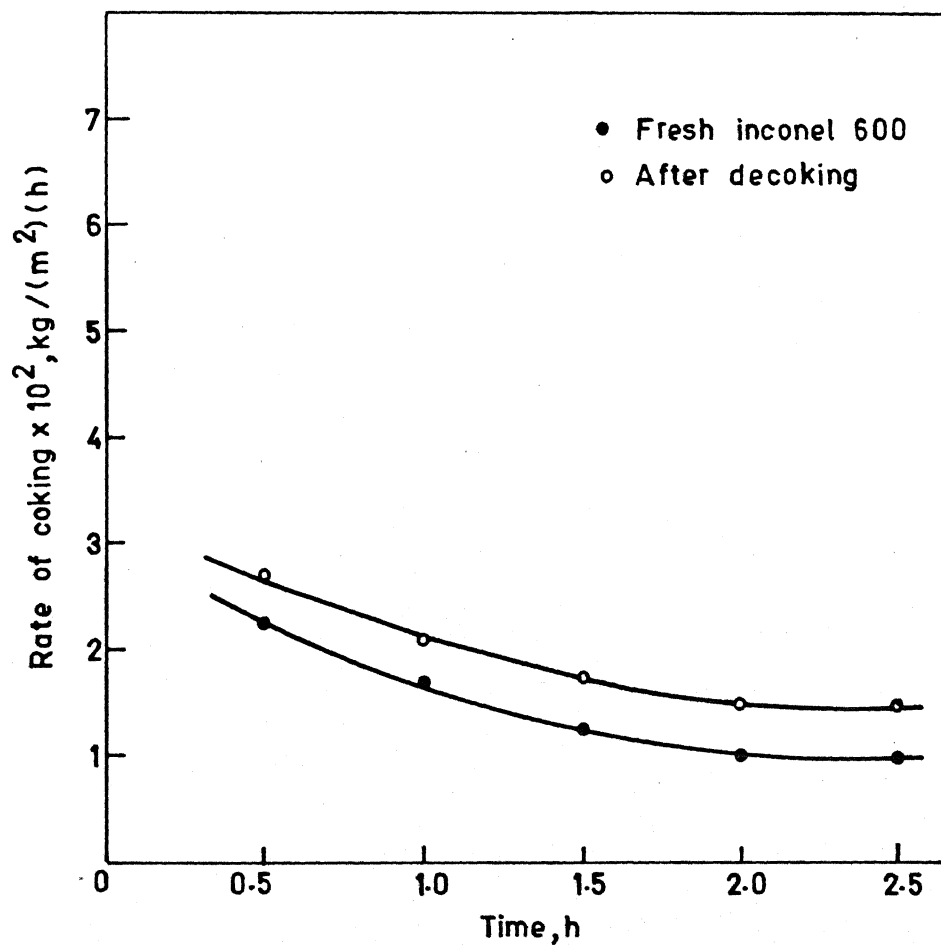


Fig. 3 Effect of decoking on the rate of formation of coke on Inconel 600 surface ($T = 1083\text{K}$, $\delta = 0.47$, $\tau = 0.49\text{s}$)

There is some controversy regarding the effect of the metal oxides on the rate of coke formation. Brown et al., (1982) mention that commercial ethylene plants normally rely on preoxidation during the steam/air decoking operation to produce a protective surface oxide film. On the other hand Brown and Albright (1976) reported that metal oxides promote secondary and undesired reactions leading to coke. Bajus et al. (1981) found that in order to achieve reproducible results, the metal oxides formed during decoking had to be removed by the action of solution of acids prior to each run. Albright and Yu (1978) reported that metal oxides on the surface are likely to favour the production of active coke.

In this study, the results were reproducible both for cleaned Inconel 600 and Inconel 600 with metal oxide present. Since the rates of coke formation were lower when the oxides had been removed by acids, all the data were taken on surfaces from which oxides had been removed.

4.3 Effect of Aromatic Concentration:

It is well known that the nature of the feedstock affects the coke deposition (Ranzi et al. 1985). Although the role of benzene and other aromatics in increasing the rate of coke formation during pyrolysis is well documented (Virk et al., 1974; Kumar and Kunzru, 1985), not much quantitative information is available regarding the effect of aromatic concentration of naphtha on coking rates. To study the effect of aromatics on

the rate of coke formation. The aromatic concentration of the naphtha feed was varied from 8.1 to 21.07 mole% by adding benzene to the naphtha. The effect of inlet aromatic concentration on the rate of coke formation is shown in Fig. 4. Rates of coke formation increased with an increase in the inlet benzene concentration. For instance, as the inlet aromatic concentration was increased from 8.1 to 21.07 mole%, the asymptotic coking rate increased by 220%. Most probably, the increase in coking rate is due to the formation of unsaturated compounds with the elimination of hydrogen in the condensed ring (Kinney and Del, 1959; Virk et al., 1974). It should be mentioned that at these conditions benzene does not pyrolyse.

To study the effect of the nature of the aromatic, one run was made with 11.49 mole% toluene, instead of benzene, added to the feed. For the same concentration the effect of toluene and benzene on the rate of coke formation was identical.

4.4 Effect of Process Variables:

The rates of coke formation varied with reactor temperature, inlet naphtha partial pressure and space time. To study the effect of temperature on coking rates the reactor temperature was varied from 1073 K to 1103 K which is the usual range for naphtha pyrolysis. Since the variation of coking rates with run time was similar to that shown in Fig. 2, only asymptotic

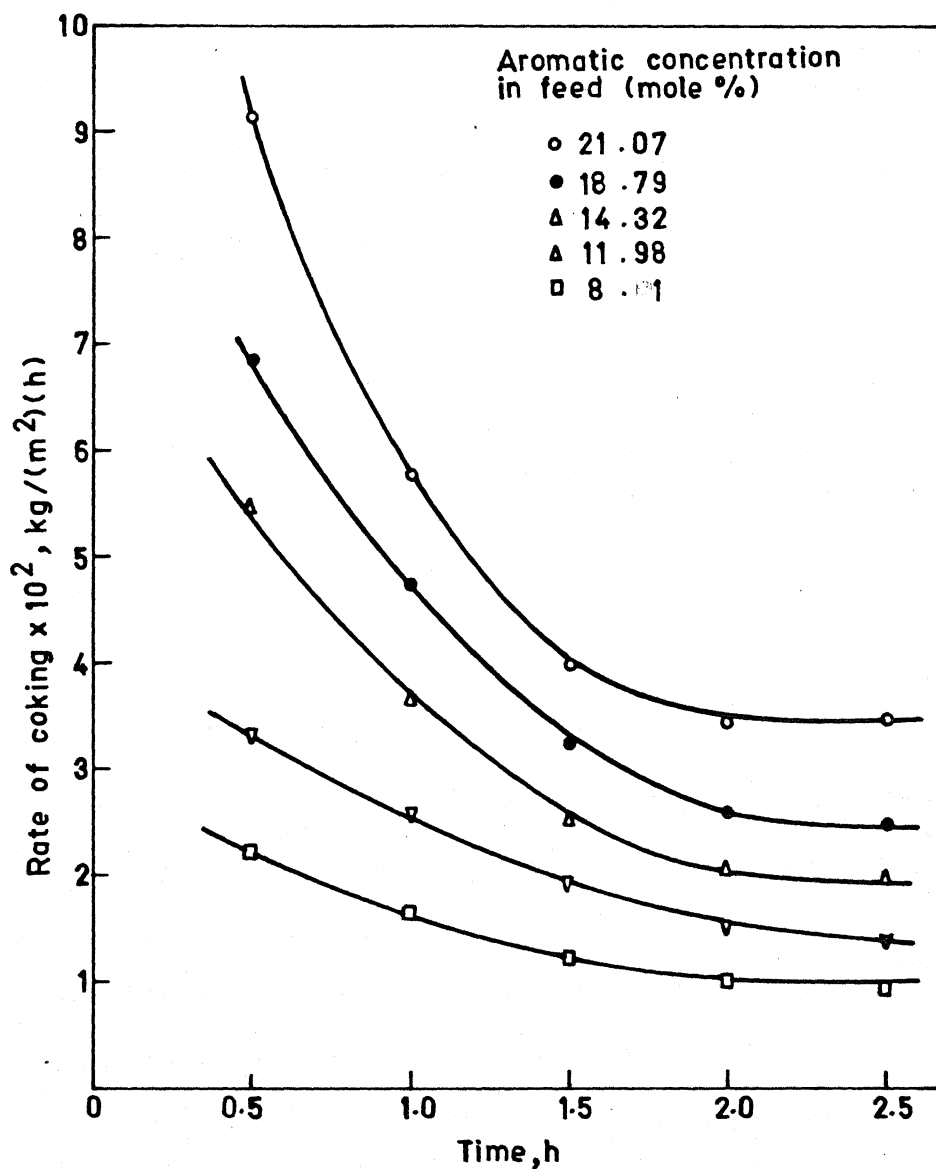


Fig. 4 Effect of inlet benzene concentration on the rate of coke deposition on Inconel 600 surface
($T = 1083\text{K}$, $\delta = 0.47$, $\tau = 0.49\text{s}$)

coking rates are being reported. The detailed variation of coking rates with time for the different runs is given in Appendix B. The variation of the asymptotic coking rate, r_a , with temperature and space time is shown in Fig. 5. Coking rates increase with increasing temperature and space time. This trend is similar to that reported for the pyrolysis of propane (Trimm and Turner, 1981a), n-hexane (Pramanik and Kunzru, 1985) and naphtha (Kumar and Kunzru, 1985). Since coke is formed from secondary reactions and once formed does not react further, rate of coking increases with temperature and space time.

The effect of inlet steam to naphtha ratio on the rate of coking at a constant temperature of 1083 K is shown in Fig. 6. With decreasing partial pressure of naphtha, the concentration of coke forming species is decreased, thus reducing the rate of coke formation. At these temperatures, the coke-steam reaction is not expected to be significant (Biba et al. 1978) and would not contribute to the reduction in rate of coking with increasing partial pressure of steam. These trends are similar to that reported by Kumar and Kunzru (1985) who used a δ of 0.71 to 1.43.

4.5 Effect of Thiophene Content of Feed:

The effect of sulfur content of the feed was studied by adding thiophene to the naphtha. The addition of various quantities of thiophene was so arranged that the wt.% of sulfur expressed as total weight of feed, varied from 0.05 to 0.5%.

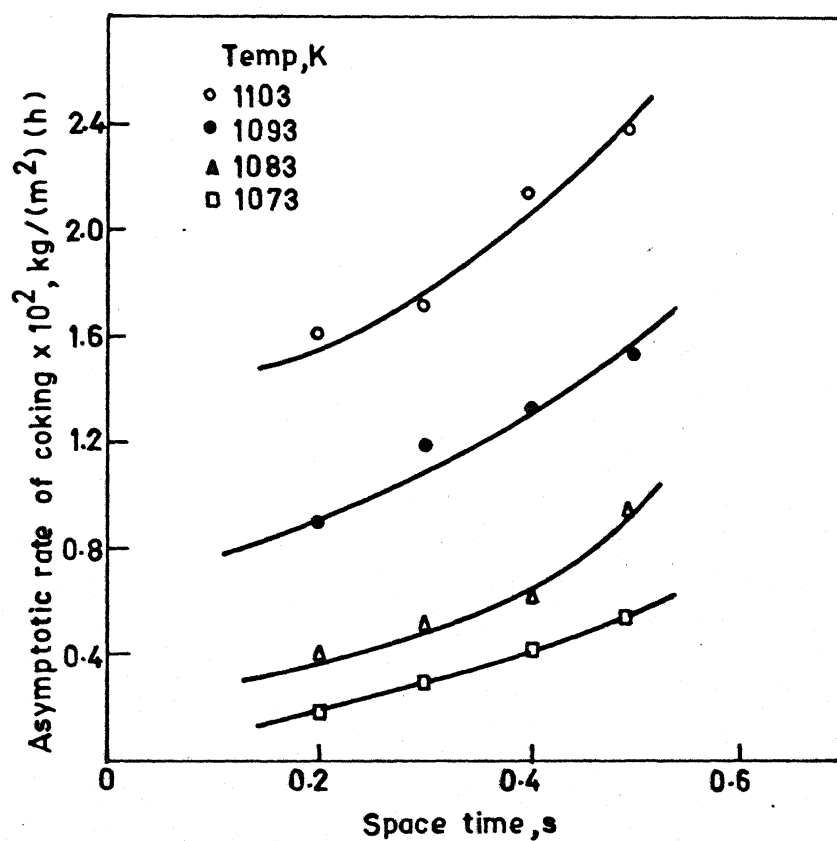


Fig. 5 Effect of temperature on asymptotic rate of coking on Inconel 600 surface ($\delta = 0.47$)

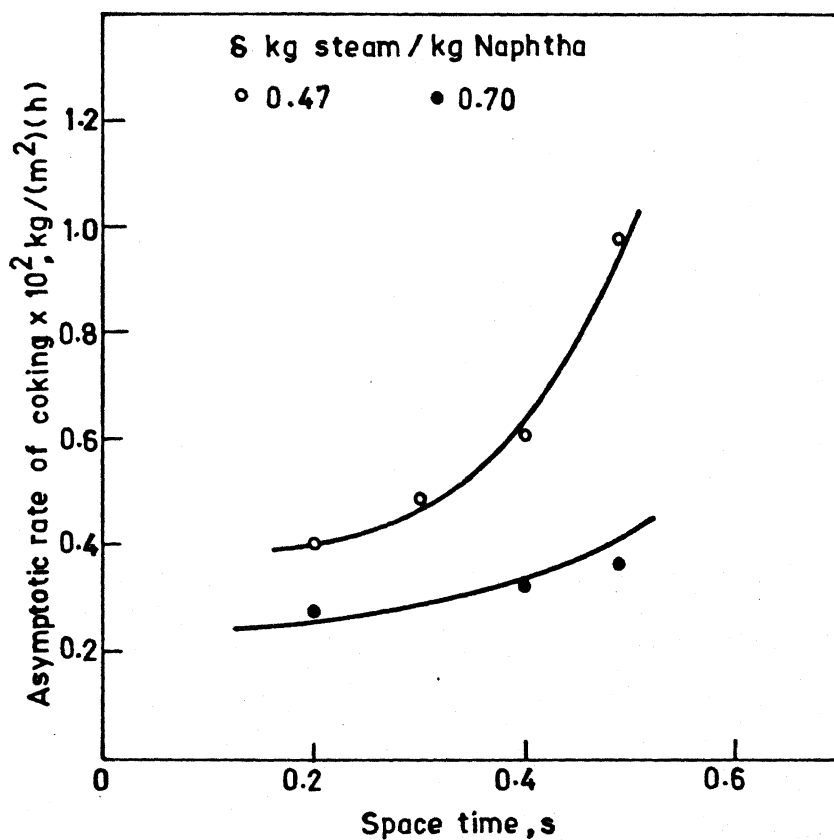


Fig.6 Effect of inlet partial pressure of naphtha on asymptotic rate of coking on Inconel 600 surface (T = 1083K)

It may be noted that the naphtha sample contains 0.05 weight % sulphur.

The addition of thiophene affected both the product yields as well as the rate of coke formation. The rate of coke formation decreased with an increase in the sulfur content of the feed and the variation with run time for different thiophene concentrations is shown in Fig. 7, whereas Fig. 8 shows the variation of the asymptotic coking rate with the thiophene content of the feed. As shown in Fig. 8, till 0.4 wt.% thiophene, the asymptotic coking rate was inversely proportional to the thiophene content of naphtha whereas at higher thiophene concentrations the inhibition in coking rate was less.

To check whether the addition of thiophene had an effect on the primary pyrolysis reaction, the total gas and liquid yields for different thiophene concentrations were measured. In addition, the aromatic content of the liquid product and the major gaseous product were also analysed. The addition of thiophene to naphtha was found to affect both the total gas and liquid yields. As shown in Fig. 9, the total gaseous yield increased whereas the total organic yields decreased with an increase in the thiophene content of the feed. The effect on the gaseous yields was highest at lower thiophene concentrations whereas between 0.4 - 1.2 wt.% thiophene, the gas yields were directly proportional to the thiophene concentration. For the range of thiophene concentration investigated,

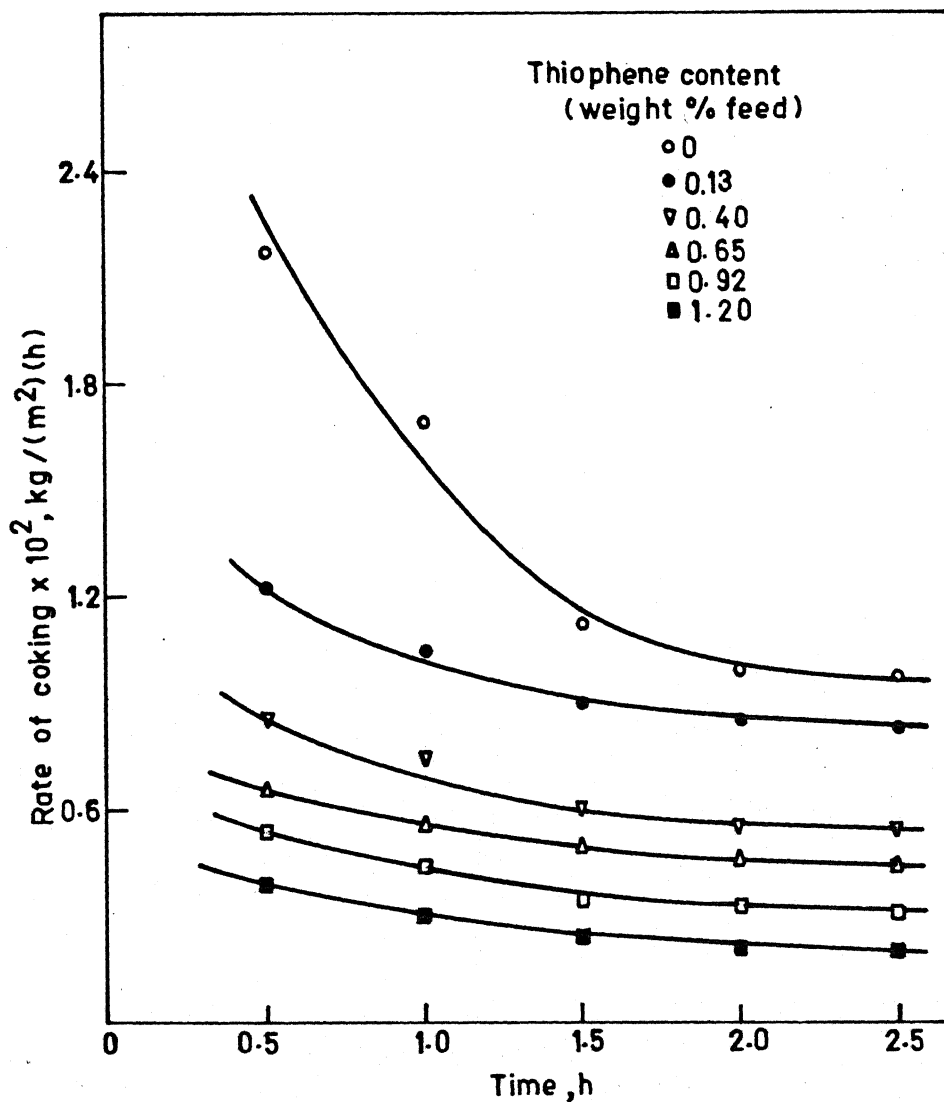


Fig. 7 Effect of thiophene on rate of coke formation on Inconel 600 surface ($T = 1083\text{K}$, $\delta = 0.47$, $\tau = 0.49\text{s}$)

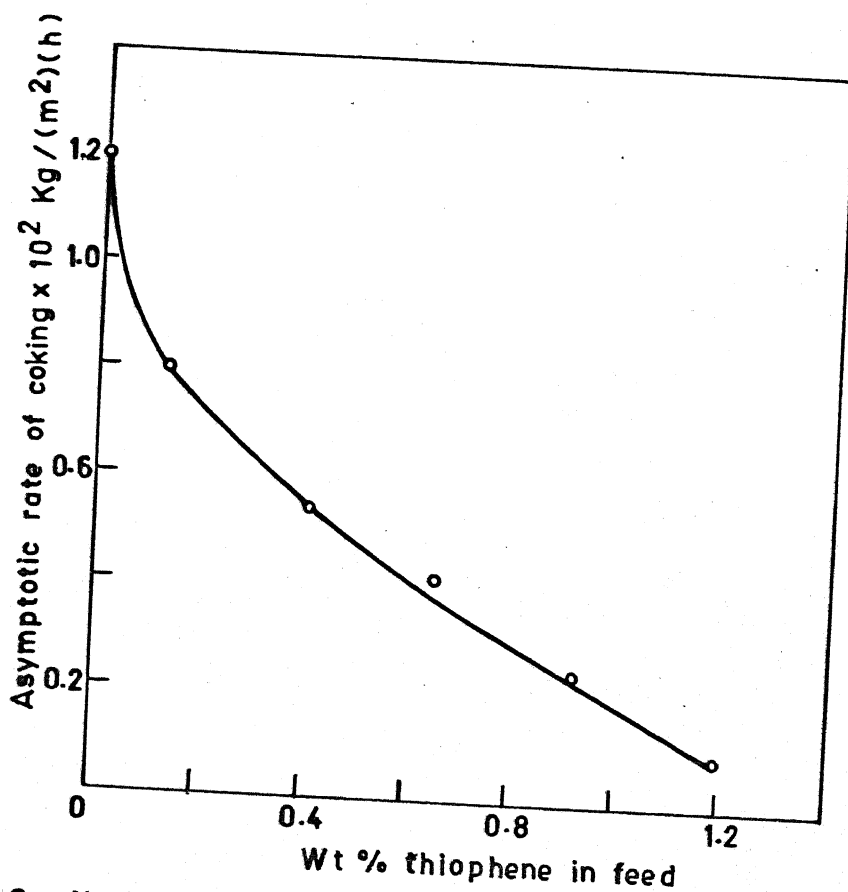


Fig. 8 Variation of asymptotic coking rate with thiophene concentration of feed

U. S. X. ANDERSON
GENERAL LIBRARY

91916

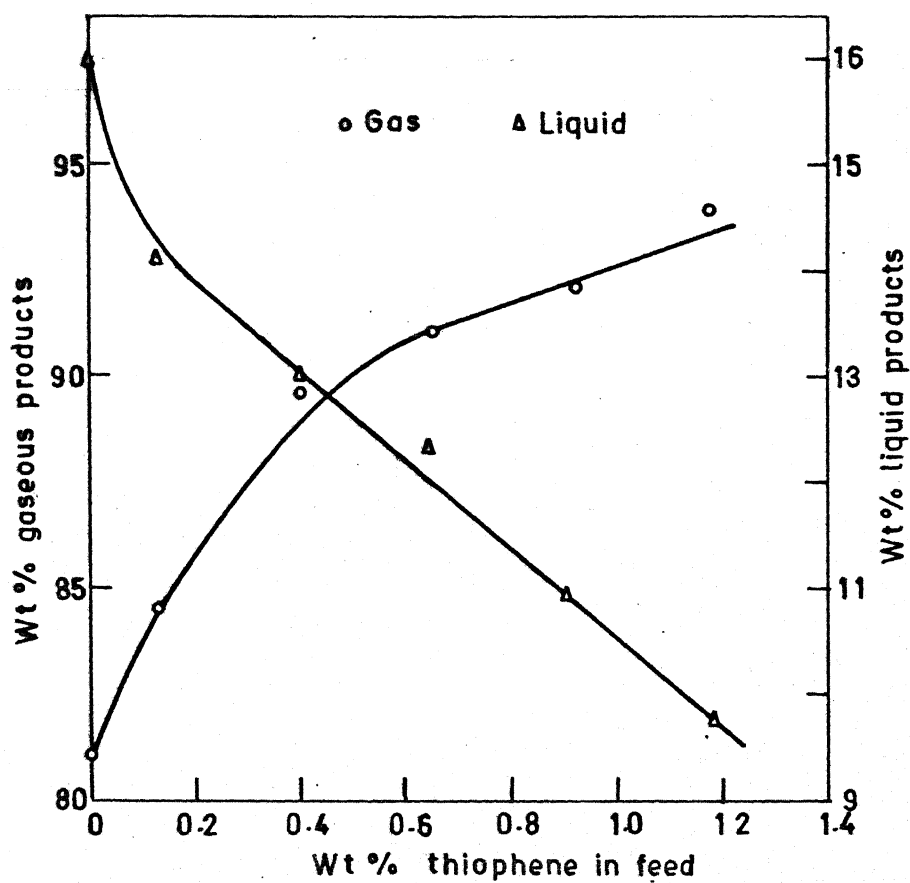


Fig. 9 Effect of thiophene concentration in naphtha on gas and liquid yields

the liquid yields were inversely proportional to the thiophene concentration of the feed.

Although the composition of the gaseous products did not change due to the addition of thiophene in the feed, the yields of the gaseous components, expressed as wt.% of naphtha feed, was higher because the total gaseous yields were higher. The effect of thiophene addition on the product yields is shown in Table 4. Addition of thiophene significantly reduced the aromatic content of the liquid product. Addition of 0.13 % thiophene in feed reduce the aromatic yield from 14.7 to 5.78 wt.%. On further addition of thiophene the decrease in the aromatic yield was less significant. As the thiophene concentration was increased from 0.13 to 1.2 wt.% the aromatic yield decreased from 5.78 to only 4.18 wt.% . It should be noted that the aromatic yield with thiophene is less than the aromatic content of the thiophene free naphtha feed, which indicates that at this temperature thiophene is reacting with the aromatics. Aromatics are very refractory and in general, do not crack during naphtha pyrolysis (VanDamme et al., 1981). However with thiophene present in the reaction mixture, the aromatics can react with S. and .SH free radical produced due to thiophene decomposition (Glass and Reid, 1929).

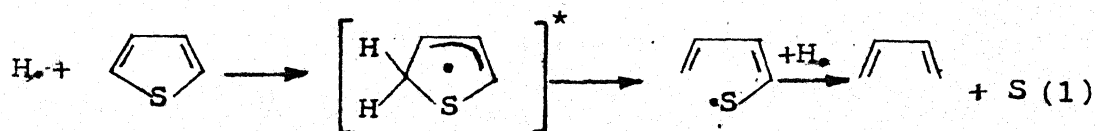
✓ The sulfur present in the feed can reduce the rate of coking in two ways. It can either react with the metal surface to form metal sulfides thus passivating the reactor walls or it

can take part in the homogeneous gas phase free radical reactions (Bajus et al., 1981). To check whether sulfur was taking part in the heterogeneous and/or homogeneous reactions one run was conducted with 1.2 wt.% thiophene in the feed and after the asymptotic coking rate had been attained, the reactor was flushed with steam and thiophene-free naphtha was passed without any intermediate decoking. It was found that the asymptotic coking rate was identical to that measured when a fresh Inconel 600 surface was used. This, together with the change in product yields, shows that thiophene is definitely taking part in the homogeneous reactions. If the reduction in rate is solely due to the presence of metal sulfides then the rate for the two cases should have been the same, because the passivating metal sulfide layer had not been removed by oxidation during decoking. The effect of sulfur in passivating the metal wall is well known (Bajus et al., 1980; Trimm and Turner, 1981b) and as such no attempt was made to confirm the presence of metal sulfides.

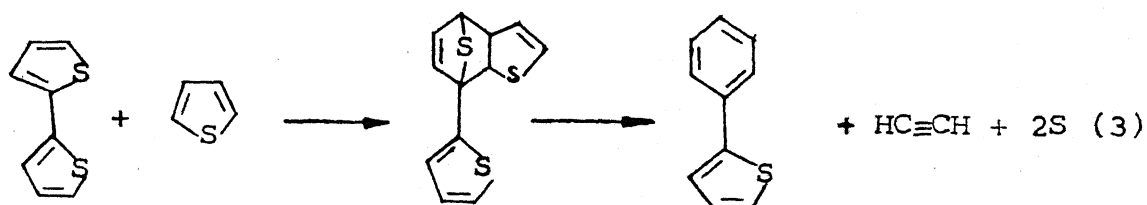
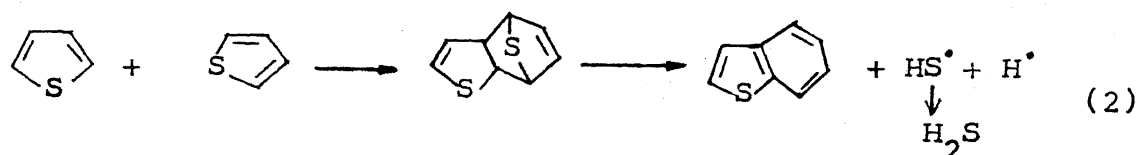
These results are in good agreement with the limited information available regarding the effect of sulfur compounds on the rate of coking. Bajus et al. (1981) studied the effect of adding thiophene to the raffinate feed and reported that addition of thiophene affected the coke formation as well as the pyrolysis. They also observed that till 0.5% thiophene, the rate of coking was inversely proportional to the thiophene

content and production of organic liquid products decreased with an increase in the thiophene content of the feed. During n-heptane pyrolysis, Bajus et al. (1981, 1983) found that the addition of thiophene, dibenzyle sulfide or dibenzyle disulfide decreased the rate of coking. At low sulfur concentration of the feed, the rate of n-heptane pyrolysis was increased whereas a further increase in the sulfur concentration decreased the rate of pyrolysis. Depeyre et al. (1985) reported the addition of sulfur compounds to n-nonane steam cracking catalyzed the rate of n-nonane decomposition and inhibited secondary reactions leading to the formation of C_2H_4 , C_4H_6 and aromatic compounds. Yields of these secondary products decreased as the weight percentage of sulfur compounds in the feed was increased. Sulfur reduced the rate of formation of coke.

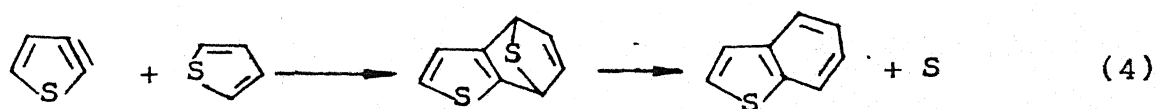
Comparison of kinetics, selectivity of decomposition and rate of coking of naphtha leads to the finding that thiophene influences both the radical conversion in the homogeneous phase and the surface reactions in the reactor. Under the given experimental conditions, reactions can occur between thiophene molecules themselves and between thiophene and the highly reactive radicals resulting from the decomposition of hydrocarbons, e.g. H. and R.



Wynberg and Bantjes (1959) pyrolyzed thiophene at 1073 - 1123 K. Among the reaction products, bithienyl as well as benzothiophene and phenylthiophene was found. The formation of these products was explained by Diels-Alder addition of thiophene itself according to the reactions (2) and (3).

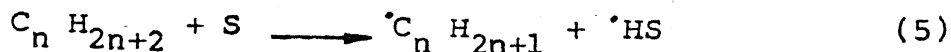


Fields and Meyerson (1967) ascribe a very important role of thiophene, which can be formed by intramolecular dehydrogenation of thiophene, as a reactive intermediate product. Reaction with a thiophene molecule could give benzothiophene according to reaction (4).

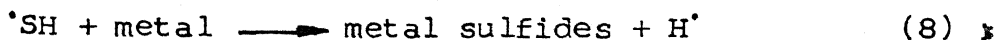
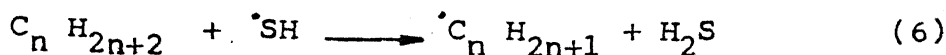


From the proposed mechanisms for the thermal conversion of thiophene, the release of sulfur (reactions 1, 3, 4) and hydrogen sulfide (reaction 2) is characteristic. Sulfur eliminated from thiophene can enter into reactions in the gaseous state. It can also react with the metal surface of the reactor. From the

possible reactions, sulfur can initiate propagation according to reaction 5 with the formation of .SH radical.



Radical $\cdot SH$ from reactions 2 and 5 can also cause propagation according to reaction 6, termination according to reaction 7 or react with the metal surface to form metal sulfides according to reaction 8.



Reactions such as (5) and (6) would increase the rate of pyrolysis of naphtha resulting in higher gaseous and lower liquid yields.

4.6 Modelling of Coke Formation:

Coke formation in the pyrolysis of naphtha is a complex phenomena due to the various possible coke forming free radical reactions and the exact mechanism is not clear.

4.6.1 Modelling of Coke Formation During Pyrolysis of Thiophene-Free-Naphtha:

Kumar and Kunzru (1985) postulated simple models involving either the reactant and/or products to model coke formation during naphtha pyrolysis. The feed was thiophene-free but the

water used contained 50 ppm CS_2 . On SS 304 surface, the asymptotic coking rate could be represented by the following expression

$$r_a = 1.68 \times 10^{23} \cdot \exp \left(\frac{-50,780}{RT} \right) C_A^{1.98} \quad (1)$$

where r_a is the asymptotic rate of coking in (kg coke)/(hr)(m²) and C_A is the concentration of the aromatics in the reactor in kg mole/m³. For this study also the applicability of relating r_a to C_A was checked. The model postulated was

$$r_a = k_o \exp \left(- \frac{E}{RT} \right) C_A^n \quad (2)$$

Since the experiment was conducted in a mixed reactor, the concentration of aromatics in the exit was the same as that inside the reactor. For calculating C_A , the molecular weight of the gaseous product was taken to be 30 (Kumar and Kunzru, 1985) and the molecular weight of the aromatic free liquid product to be 91. Since the total volumetric flow rate of the gaseous product and the mass flow rate of the liquid product was experimentally measured, C_A could be calculated as,

$$C_A = \frac{\text{moles of aromatics}}{\text{moles of aromatics} + \text{moles of aromatic free product} + \text{moles of water} + \text{moles of gaseous product}}$$

For all the runs, the molar flow rate of the aromatic - free product constituted only from 2.0 to 4.0% of the total molar flow rates. As shown in Fig. 10, it was possible to relate r_a for all the runs with C_A . It should be emphasized

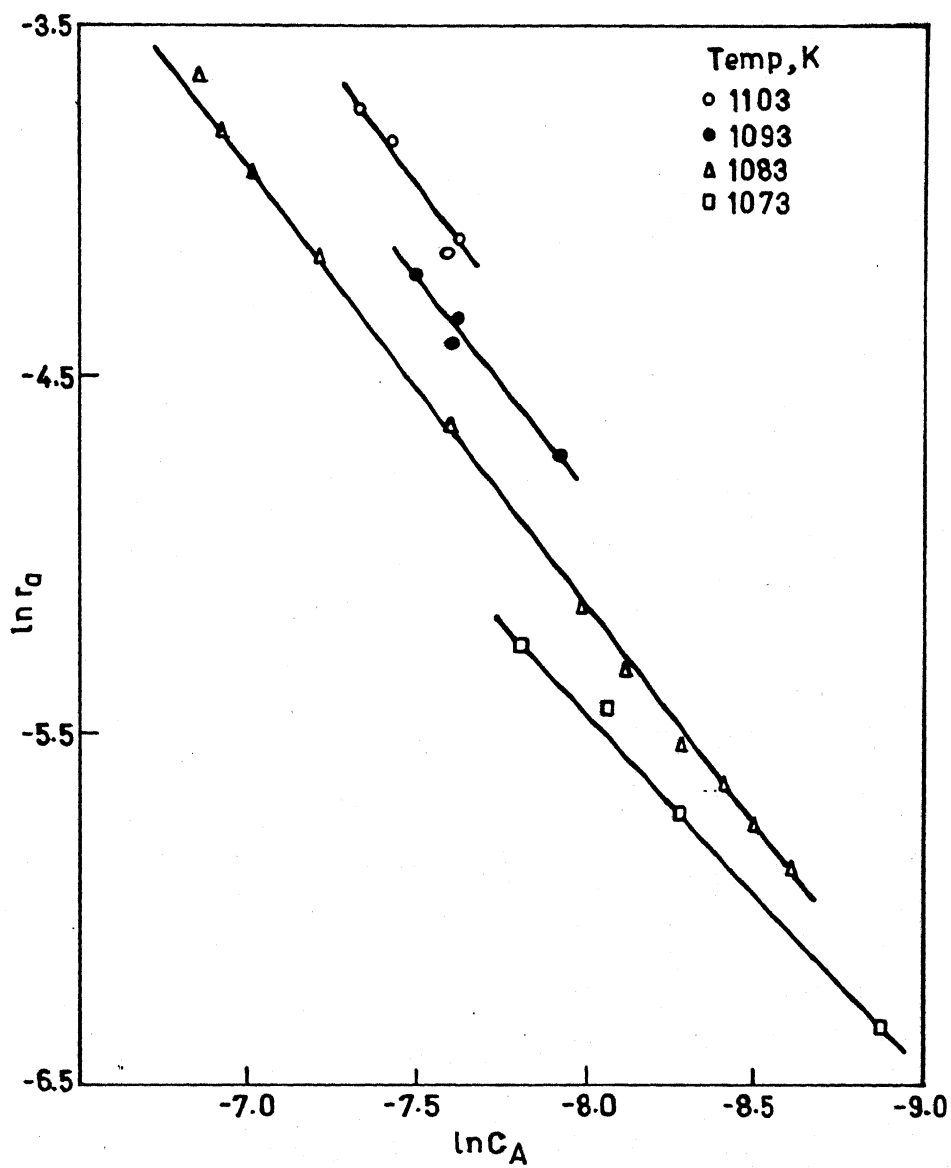


Fig.10 Determination of reaction order for rate of coking at different temperatures

that the points shown in Fig. 10 were taken at various temperatures, space times, δ , and inlet benzene concentration of the feed.

The initial estimates of k_0 , E and n were obtained graphically using linearization. To estimate the order of the reaction $\ln r_a$ vs $\ln C_A$ was plotted for various temperatures and the plot is shown in Fig. 10. The reaction order for coking varies from 1.0 to 1.4 and the average order for the rate was 1.29. However, for modelling purposes the value of n was taken to be a constant. The rate constants at different temperatures were obtained from the slopes of the plot between r_a and $C_A^{1.29}$, as shown in Fig. 11. The value of the activation energy using linear analysis was obtained by an Arrhenius plot, Fig. 12, of $\ln k$ vs $1/T$, and the value was found to be 58.2 kcal/gmole.

The parameters of expression (2) i.e. E , k_0 and n were estimated by nonlinear optimization using data for 23 runs and the tabulated values of r_a , T and C_A are shown in Table 5. The objective function was chosen to be

$$\sum [(r_a)_{\text{cal.}} - (r_a)_{\text{expt.}}]^2$$

where $(r_a)_{\text{cal.}} = k_0 \exp\left(-\frac{E}{RT}\right) C_A^n$

The objective function was minimized by the appropriate choice of frequency factor, activation energy and reaction order. The initial estimates of these parameters were taken from the linear

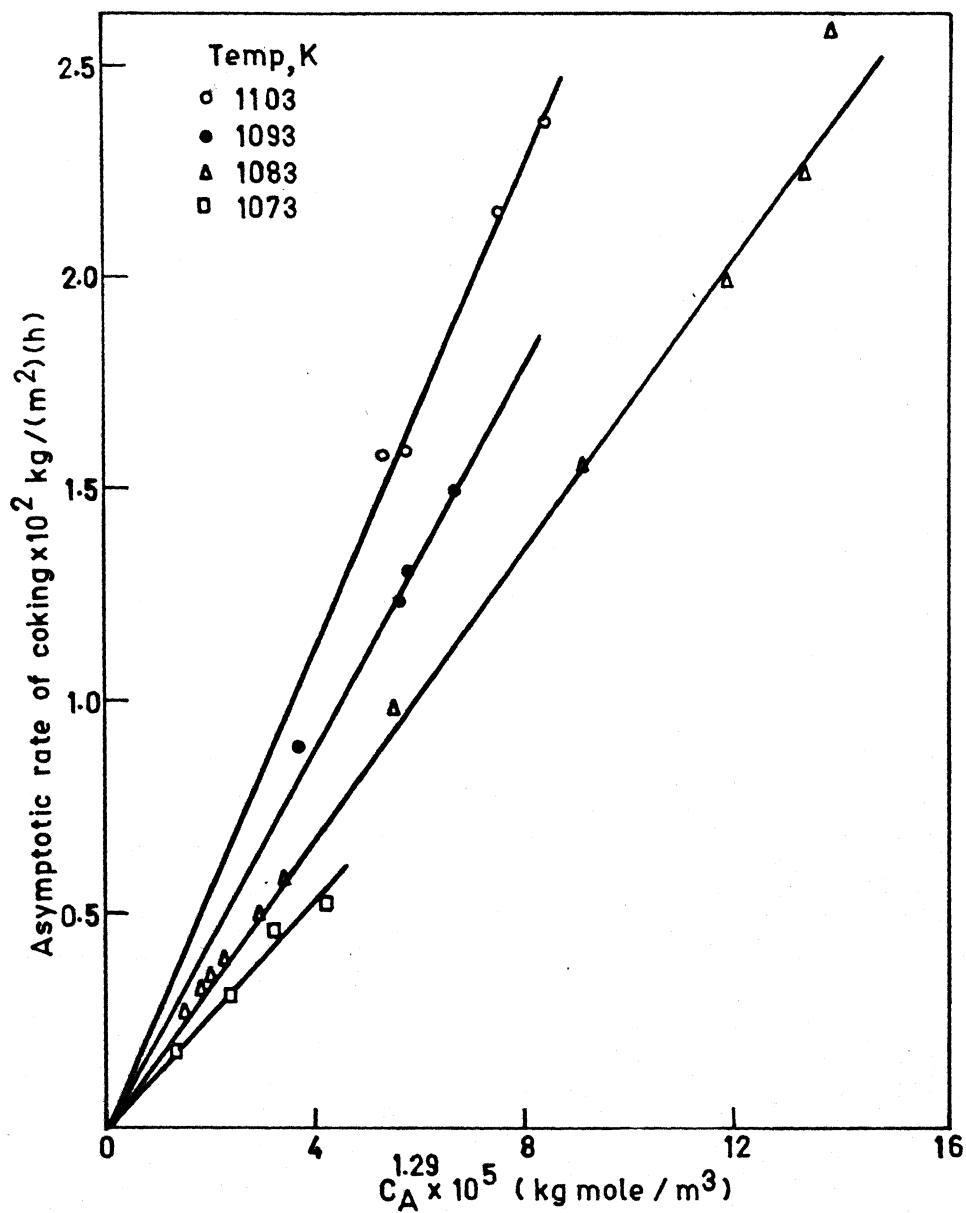


Fig.11 Determination of rate constant for asymptotic rate of coking at different temperatures

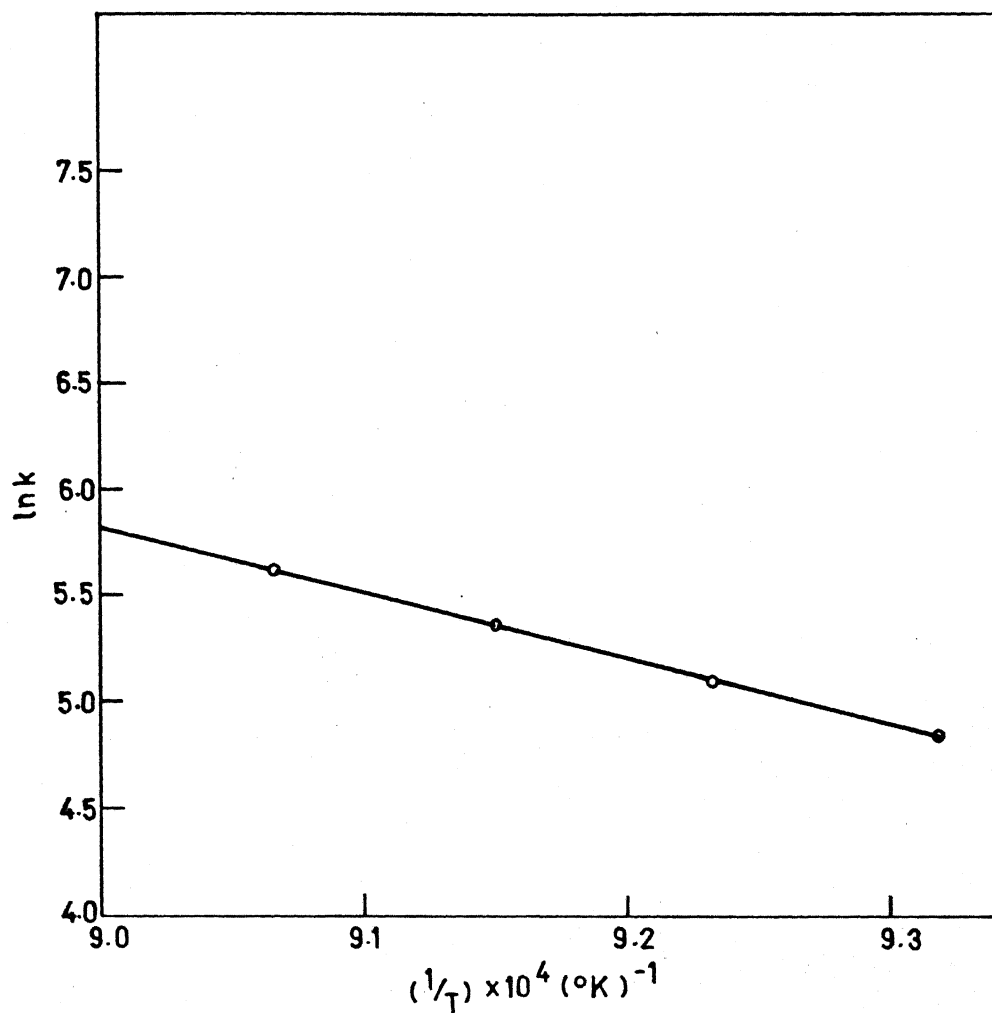


Fig.12 Arrhenius plot for the deposition of coke

Table 5: Effect of Process Variables on the Rate of Coking of Thiophene Free Naphtha

Run No.	T, K	τ , s	$\delta \frac{\text{Kg steam}}{\text{Kg naphtha}}$	$C_A \times 10^4 \frac{\text{Kg mole}}{\text{m}^3}$	$r_a \times 10^2 \frac{\text{Kg}}{\text{m}^2 \text{ h}}$
1	1073	0.20	0.47	1.39	0.18
2	1073	0.30	0.47	2.48	0.33
3	1073	0.40	0.47	3.07	0.44
4	1073	0.49	0.47	4.04	0.53
5	1083	0.20	0.47	2.47	0.40
6	1083	0.30	0.47	2.97	0.49
7	1083	0.40	0.47	3.39	0.59
8	1083	0.49	0.47	4.95	0.99
9	1093	0.20	0.47	3.61	0.90
10	1093	0.30	0.47	5.01	1.23
11	1093	0.40	0.47	4.88	1.32
12	1093	0.49	0.47	5.53	1.50
13	1103	0.20	0.47	5.06	1.60
14	1103	0.30	0.47	4.88	1.65
15	1103	0.40	0.47	5.88	2.17
16	1103	0.49	0.47	6.75	2.35
17	1083	0.20	0.70	1.79	0.28
18	1083	0.40	0.70	2.03	0.32
19	1083	0.49	0.70	2.22	0.36
20	1083	0.49	0.47	7.37	1.55
21	1083	0.49	0.47	9.01	2.00
22	1083	0.49	0.47	9.83	2.25
23	1083	0.49	0.47	10.07	2.60

analysis. The optimization method used was a combined Gauss-Newton and quasi-Newton subroutine. The calculations were done on a DEC 1090 system and the detailed computer listing is given in Appendix C. Due to the strong correlation between the frequency factor and activation energy, a reparameterization was necessary. For the reparameterization, the rate constant was expressed as

$$k_0 = (k'_0 \cdot e^{-\frac{E}{RT_m}}) e^{-\frac{E}{R}(\frac{1}{T} - \frac{1}{T_m})}$$

where T_m is the average temperature for all the runs. The value of k_0 , E and n obtained by nonlinear optimization together with the 95% confidence limits are shown in Table 6. The comparison between the experimental and calculated rate using this model is shown in Fig. 13. The average percent deviation, calculated as

$$\frac{1}{N} \sum \left(\frac{|(r_a)_{\text{cal.}} - (r_a)_{\text{expt.}}|}{(r_a)_{\text{expt.}}} \right) \times 100$$

was 6.0% and the maximum error between the predicted and experimental coking rate was 22%. Using non-linear regression the activation energy and reaction order were found to be 58.5 kcal/mole and 1.32, respectively. Compared to the values reported by Kumar and Kunzru (1985), the activation energy is higher whereas the value of the reaction order is lower. The difference could be due to two reasons. Firstly, the metal surface used in the two studies were different and secondly, in their study, the water used for steam generation contained

Table 6: Parameter Estimates for the
Non-linear Coking Model

Frequency factor $\frac{\text{Kg coke}}{(\text{m}^2)(\text{hr}) \cdot (\frac{\text{Kg mole}}{\text{m}^3})^n}$	Activation energy kcal/mole	n	RSS
$(1.53 \pm 0.96) \times 10^{14}$	58.5 ± 7.5	1.32 ± 0.09	1.34×10^{-5}

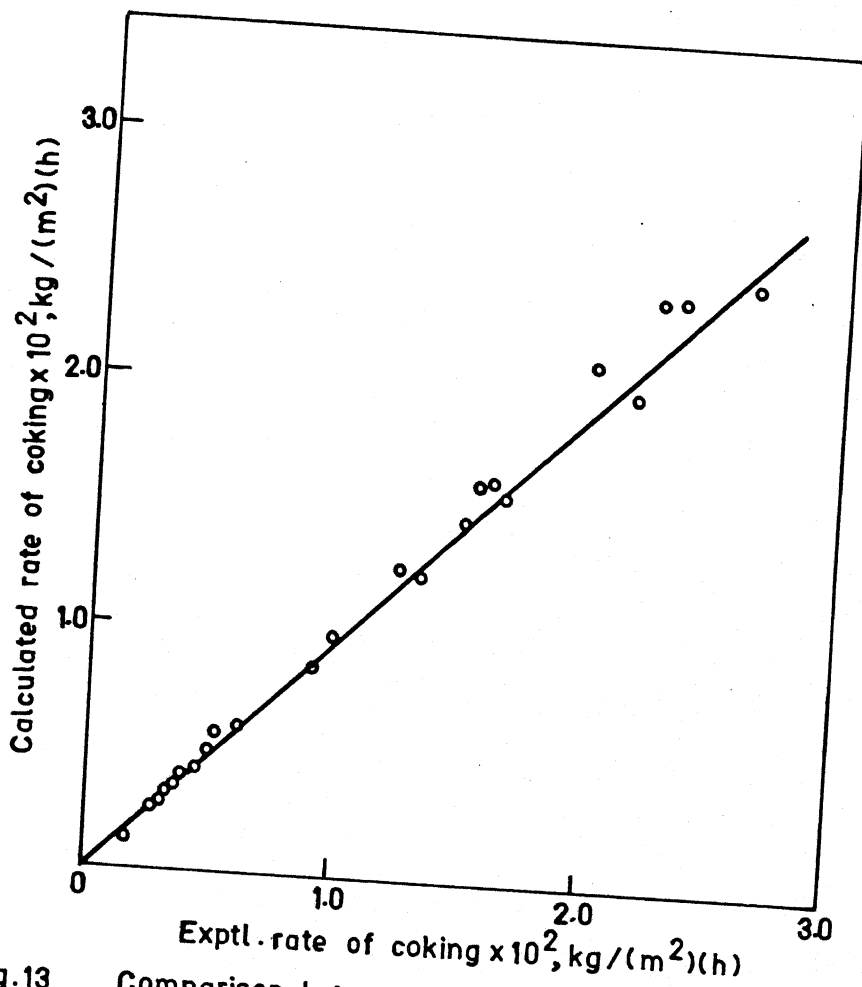


Fig.13 Comparison between calculated and experimental asymptotic rates of coking

50 ppm CS_2 . The presence of S in feed water can definitely influence the order of the reaction as was found in this study as discussed below.

4.6.2 Modelling of Coke Formation During Pyrolysis of Thiophene Containing Naphtha:

All the runs for rate of coking in the presence of thiophene were taken at a constant temperature. It was found that for thiophene- containing feed, the rate of coking could also be related to the aromatic concentration. The order of the reaction for coking was found by a linear plot of $\ln r_a$ vs $\ln C_A$ as shown in Fig. 14. The order of reaction was found to be 2.2, which show that the presence of thiophene increases the reaction order for coking. This order is comparable to the value of 1.98 reported by Kumar and Kunzru (1985) for CS_2 present in the system. It seems that the radicals produced due to thiophene decomposition take part in the homogeneous and/or heterogeneous reactions to increase the order. Due to the large number of free radicals reactions taking place during naphtha pyrolysis, nothing can be said about the exact mechanism by which this occurs.

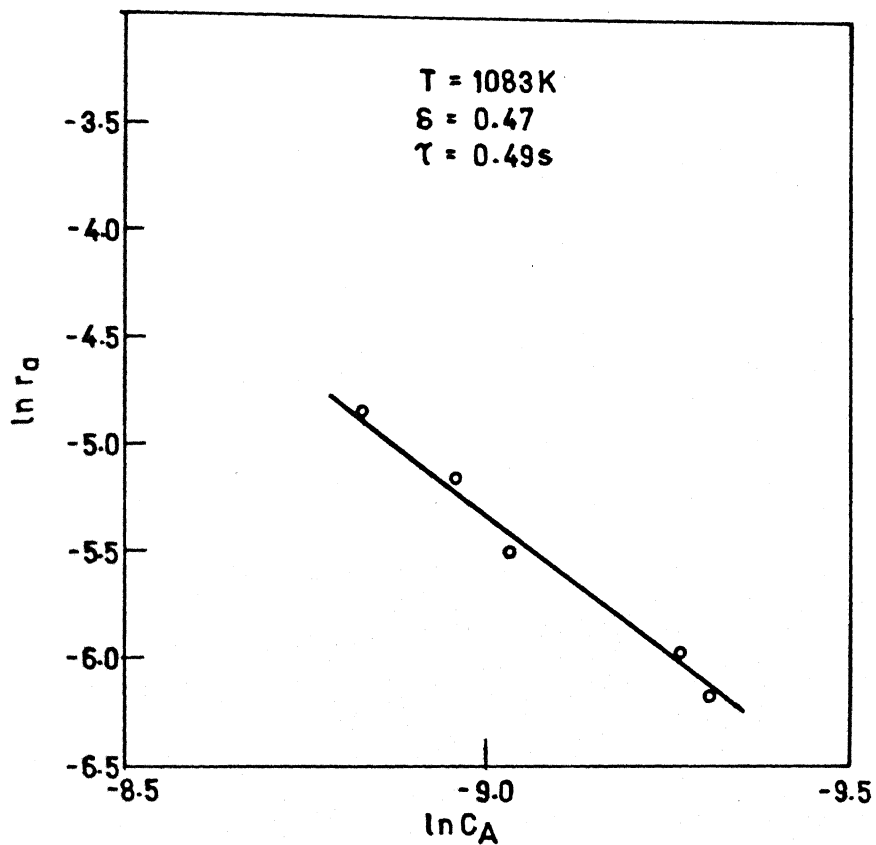


Fig. 14 Effect of inlet thiophene concentration on reaction order for rate of coke formation

CHAPTER 5

CONCLUSIONS AND RECOMMENDATION

5.1 Conclusion:

Based on the results of this study, the following conclusions can be made:

1. The rate of coke formation is lowest on Inconel 600 surface in comparison with SS 304 and SS 316.
2. The presence of metal oxides formed on the reactor surface during decoking promote the rate of coke formation.
3. Rate of coke formation increases with an increase in aromatic concentration of the feedstock.
4. Rate of coke formation increases with an increase in the reactor temperature and space time but decreases as the inlet steam to naphtha ratio is increased.
5. Rates of coke formation decrease with increasing thiophene concentration of the feed.
6. The coking model developed in this study in the absence of thiophene in the feed can be represented

as

$$r_a = (1.533 \times 10^{14}) \exp \left(- \frac{58,500}{RT} \right) (C_A)^{1.32}$$

7. The variation of the asymptotic coking rate in the presence of thiophene can be expressed as an approximately second order reaction involving the aromatics.

5.2 Recommendation:

The following recommendations are proposed for further study:

1. A detailed analysis of the C_4 and liquid products should be attempted to further improve the model.
2. The naphtha pyrolysis can be conducted on swaged coils and the validity of the main pyrolysis and coking models can be checked for such coils. Moreover, the effect of varying diameter may be studied for coking rates.
3. Sulfur effect on naphtha should be checked more rigorously by analysing in detail the liquid and gaseous products and measuring rates of coke formation at various temperature for naphtha mixed with thiophene.

REFERENCES

Albright, L.F.; Mc-Connell, C.F., "Deposition and Gasification of Coke during Ethane Pyrolysis", Paper presented 175th ACS National Mtg., Annaheim, Calif., March 1978.

Albright, L.F.; Yu, Y.C. and Welther, K., Proc. 85th American Institute of Chemical Engineers National Mtg., 4th June, 1978.

Albright, L.F.; Mc-Connell, C.F. and Welther, K., 'Thermal Hydrocarbon Chemistry', Editors, A.G. Oblad, H.G. Davis and R.T. Eddinger, Advances in Chemistry Series No. 188, p. 175, Amer. Chem. Soc. Washington, D.C. 1979.

Albright, L.F. and Yu, Yu-Hung Carol., "Pyrolysis of Acetylene, Butadiene and Benzene in Different Tubular Reactors", Paper presented 175th ACS National Mtg., Annaheim, Calif., March 1978.

Bajus, M. and Vesley, V., Ind. Eng. Chem. Prod. Res. Dev., 18, 30, 1979.

Bajus, M., Vesely, V., Leciercq, P.A. and Rijks, J.A., 'Steam Cracking of Hydrocarbons. 3. Straight-Run Naphtha', Ind. Eng. Chem. Prod. Res. Dev. 19, 556, 1980.

Bajus, M.; Vesely, V., Baxa, J., Leclercq, P.A. and Rijks, J.A., 'Steam Cracking of Hydrocarbons. 5. Effect of Thiophene on Reaction Kinetics and Coking', Ind. Eng. Chem. Prod. Res. Dev., 20, 741, 1981.

Bajus, M., Baxa, J., Leclercq, P.A. and Rijks, J.A., 'Steam Cracking of Hydrocarbons. 6. Effect of Dibenzyl Sulfide and Dibenzyl Disulfide on Reaction Kinetics and Coking', Ind. Eng. Chem. Prod. Res. Dev. 22, 335, 1983.

Biba, V.; Macak, J.; Klose, E. and Malecha, J., Ind. Eng. Chem. Proc. Des. Dev., 17, 92, 1978.

- Brown, S.M. and Albright, L.F., 'Industrial and Laboratory Pyrolysis', ACS Symposium Series, 32, Chapter 17, 1976.
- Brown, D.E.; Clark, J.T.K.; Foster, A.I.; Mc Carroll, J.J. and Sims, M.L., 'Inhibition of Coke formation in Ethylene Steam Cracking', American Chemical Society, 1982.
- Depeyre, D.; Filcoteaux, C.; Blouri, B. and Ossebl, J.G., 'Pure n-Nonane Steam Cracking and the Influence of Sulphur Compounds', Ind.Eng.Chem.Proc.Des.Dev., 24, 920, 1985.
- Eisenberg, B. and Bliss, H., 'Recent Advances in Kinetics', Chem. Engg. Symp. Series, 67, 1, 1967.
- Ebert, K.H.; Edlerer, H.J. and Isbern, G., Int.J. Chem. Kin., 15, 475, 1983.
- Frey, F.E. and Hepp, H.J., Ind.Eng.Chem. 25, 441, 1933.
- Froment, G.F. and Bischoff, K.B., Chem.Eng.Sci., 34, 635, 1961.
- Fields, E.K. and Meyerson, S., In 'Organic Sulphur Chemistry', Janssen, M.J., Ed., Interscience, New York, 1967.
- Glass, H.B. and Reid, E.E., J.Am. Chem.Soc., 51, 3428, 1929.
- Hirt, T.J. and Palmer, H.B., Carbon, 1, 201, 1967.
- Johnson, G.L. and Anderson, R.C., Proc. 5th Carbon Conf., Vol. 1, 395, Pergamon Press, Oxford (1972).
- Kumar, P. and Kunzru, D., 'Modelling of Naphtha Pyrolysis', Ind.Eng.Chem. Prod. Res.Dev., 24, 774, 1985.
- Kunzru, D.; Shah, Y.T. and Stuart, E.B., Ind.Eng.Chem. Proc. Des. Dev., 12, 339, 1973.
- Kunzru, D.; Shah, Y.T. and Stuart, E.B., Ind.Eng.Chem. Proc. Des.Dev., 11, 605, 1972.

- Kinney, C.R. and Del Bel, E., *Ind. Eng. Chem.*, 46, 548, 1959.
- Mandal, T.K., "Catalytic Gasification of Coke During the Pyrolysis of n-Hexane", M.Tech. Thesis, submitted to Dept. of Chem. Engg., I.I.T., Kanpur, 1984.
- Newsome, D.S. and Leftin, H.P., 'Coking Rates in a Laboratory Pyrolysis Furnace', Paper presented at 72nd Annual A.I.Ch.E. Mtg., San Francisco, Calif., Nov. 25-29, 1979.
- Pramanik, M. and Kunzru, D., 'Coke Formation in the Pyrolysis of n-Hexane', *Ind. Eng. Chem. Prod. Res. Dev.* 24, 1275, 1985.
- Ranzi, E., Dente, M., Pierucci, S., Barendregt, S. and Cronin, P., 'Coking Simulation Aids on-Stream Time', *Oil and Gas Journal*, Sept. 2, 49, 1985.
- Shah, Y.T.; Stuart, E.B. and Sheth, K.D., *Ind. Eng. Chem. Proc. Des. Dev.*, 15, 518, 1976.
- Silcocks, C.G., *Proc. Roy. Soc. (London)*, A 233, 465 1956.
- Snow, R.H., Peck, R.E. and Von Fredersdroff, C.G., *A.I.Ch.E. J.*, 5, 304, 1959.
- Steacia, F.W.R. and Puddington, I.E., *Can. J. Research*, 16B, 176, 1938.
- Sandler, S. and Chung, Yu-Ho, *Ind. Eng. Chem. Prod. Res. Dev.*, 53, 391, 1961.
- Sundaram, K.M. and Froment, G.F., *Chem. Eng. Sci.*, 34, 635, 1979.
- Sundaram, K.M., Van Damme, P.S. and Froment, G.F., *A.I.Ch.E. J.*, 27, 946, 1981.
- Trimm, D.L. and Turner, C.J., 'The Pyrolysis of Propane. I. Production of Gases, Liquids and Carbon', *J. Chem. Tech. Biotechnol.*, 31, 195, 1981a.

Trimm, D.L. and Turner, C.J., 'The Pyrolysis of Propane, II. Effect of Hydrogen Sulfide', J. Chem. Tech. Biotechnol. 31, 285, 1981b.

Vokan, A.G. and April, G.C., Ind. Eng. Chem. Proc. Des. Dev., 16, 429, 1977.

Virk, P.S.; Chambers, L.E. and Woebeke, H.N., Adv. Chem. Ser. 131, 237, 1974.

Van Damme, P.S.; Froment, G.F. and Balthasar, W.B., Ind. Eng. Chem. Proc. Des. Dev., 20, 366, 1981.

Wynberg, H. and Bantjes, A., J. or G. Chem. 24, 1421, 1959.

APPENDIX A

Calibration Details of Various Columns

Sl No.	Component	Peak area per c.c., (Duropak column)	Peak area per c.c. (Poropak-Q column)	Peak area per microlitre , (25% DEGS on chromosorb-P column)
1.	Hydrogen	-	106666	-
2.	Methane	-	213333	-
3.	Ethane	-	24166	-
4.	Ethylene	-	15000	-
5.	Propylene	44,000	-	-
6.	n-Butane	79,500	-	-
7.	Benzene	-	-	107500
8.	Toluene	-	-	117500
9.	Xylene	-	-	231610

APPENDIX BRates of Coke Formation with Run Time at Different
Temperatures and Space Time

1. Temperature = 1073 K

$$\delta = 0.47 \frac{\text{Kg steam}}{\text{Kg naphtha}}$$

Space time, s	Run time, h	Rate of coking, $\times 10^2$ $\frac{\text{Kg}}{\text{m}^2 \text{ hr}}$
0.20	0.5	0.27
	1.0	0.23
	2.0	0.20
	2.5	0.18
0.30	0.5	0.40
	1.0	0.36
	2.0	0.33
	2.5	0.32
0.40	0.5	0.48
	1.0	0.48
	2.0	0.44
	2.5	0.44
0.49	0.5	0.69
	1.0	0.58
	2.0	0.50
	2.5	0.53

2. Temperature = 1083 K

$$\delta = 0.47 \frac{\text{Kg steam}}{\text{Kg naphtha}}$$

Space time, s	Run time, h	Rate of coking x 10 ² , $\frac{\text{Kg}}{\text{m}^2 \text{ hr}}$
0.20	0.50	0.81
	1.0	0.72
	2.0	0.45
	2.5	0.40
0.30	0.5	1.00
	1.0	0.82
	2.0	0.50
	2.5	0.49
0.40	0.5	1.32
	1.0	1.05
	2.0	0.61
	2.5	0.59
0.49	0.5	1.55
	1.0	1.20
	2.0	1.00
	2.5	0.99

3. Temperature = 1093 K

$$\delta = 0.47 \frac{\text{Kg steam}}{\text{Kg naphtha}}$$

Space time, s	Run time, h	Rate of coking x 10 ² ,
		$\frac{\text{Kg}}{\text{m}^2 \text{ hr}}$
0.20	0.5	1.05
	1.0	0.98
	2.0	0.92
	2.5	0.90
0.30	0.5	1.50
	1.0	1.37
	2.0	1.25
	2.5	1.23
0.40	0.5	1.70
	1.0	1.45
	2.0	1.34
	2.5	1.32
0.49	0.5	2.10
	1.0	1.85
	2.0	1.52
	2.5	1.50

4. Temperature = 1103 K

$$\delta = 0.47 \frac{\text{Kg steam}}{\text{Kg naphtha}}$$

Space time, s	Run time, h	Rate of coking x 10 ² , $\frac{\text{Kg}}{\text{m}^2 \text{ hr}}$
0.20	0.5	1.80
	1.0	1.75
	2.0	1.59
	2.5	1.60
0.30	0.5	2.00
	1.0	1.80
	2.0	1.68
	2.5	1.65
0.40	0.5	2.65
	1.0	2.40
	2.0	2.20
	2.5	2.17
0.49	0.5	2.76
	1.0	2.58
	2.0	2.33
	2.5	2.35

APPENDIX C

Computer Program for the Nonlinear Least
Square Estimation of Model Parameters


```

T(13,1)=1./1103.
T(13,2)=5.067E-04
Y(13)=1.5E-02
T(14,1)=1./1103.
T(14,2)=4.88E-04
Y(14)=1.55E-02
T(15,1)=1./1103.
T(15,2)=5.88E-04
Y(15)=2.17E-02
T(16,1)=1./1103.
T(16,2)=6.755E-04
Y(16)=2.35E-02
T(17,1)=1./1083.
T(17,2)=1.79E-04
Y(17)=0.28E-02
T(18,1)=1./1083.
T(18,2)=2.034E-04
Y(18)=0.32E-02
T(19,1)=1./1083.
T(19,2)=2.2223E-04
Y(19)=0.36E-02
T(20,1)=1./1083.
T(20,2)=7.37E-04
Y(20)=1.55E-02
T(21,1)=1./1083.
T(21,2)=9.005E-04
Y(21)=2.00E-02
T(22,1)=1./1083.
T(22,2)=9.83E-04
Y(22)=2.25E-02
T(23,1)=1./1083.
T(23,2)=10.07E-04
Y(23)=2.60E-02

```

```

LIW=1
LW=300
IFAIL=1
CALL E04GCF(M,N,X,FSUMSQ,IW,LIW,W,LW,IFAIL)
IF(IFAIL.NE.0)WRITE(NOUT,9998)IFAIL
IF(IFAIL.EQ.1)GOTO 40
WRITE(NOUT,9997)FSUMSQ
WRITE(NOUT,9996)(X(J),J=1,N)
CALL LSFUN2(M,N,X,FVEC,FJAC,23)
DO 131 I=1,M
  YC(I)=Y(I)+FVEC(I)
  WRITE(5,132)I,YC(I)
  WRITE(30,132)I,YC(I)
  FORMAT(6X,'YC(',I2,')=',E12.5)
CONTINUE
DO 121 I=1,N
  DO 121 J=1,N
    A(I,J)=0.0
  DO 122 K=1,M
    A(I,J)=A(I,J)+FJAC(K,I)*FJAC(K,J)
  CONTINUE
DO 600 I=1,N
  WRITE(NOUT,85) (A(I,J),J=1,N)
CALL STADEV(X,A,N,M,FSUMSQ)
WRITE(NOUT,9994)
STOP

```

```

FORMAT(///,16H ERROR EXIT TYPE,I3,22H _ SEE ROUTINE DOCUMENT,1HT)
FORMAT(///,31H ON EXIT,THE SUM OF SQUARES IS,F12.4)
FORMAT(13H AT THE POINT,3F12.4)
FORMAT(6A4,1A3)
FORMAT(10X,6(2X,E12.5))
END

```

```

-----
SUBROUTINE LSFUN2(M,N,X,FVECC,FJACC,LJC)
INTEGER LJC,M,N
REAL FJACC(LJC,N),FVECC(M),X(N)
REAL T(23,2),Y(23)
INTEGER I
COMMON Y,T
DO 20 I=1,M
C=1./1088.
FVECC(I)=X(1)*EXP(X(2)*(T(I,1)-C))*(T(I,2)**X(3))-Y(I)
FJACC(I,1)=EXP(X(2)*(T(I,1)-C))*(T(I,2)**X(3))
FJACC(I,2)=X(1)*(T(I,1)-C)*EXP(X(2)*(T(I,1)-C))*(T(I,2)**X(3))
FJACC(I,3)=X(1)*EXP(X(2)*(T(I,1)-C))*(T(I,2)**X(3))*ALOG(T(I,2))
CONTINUE
DO 779 I=1,M
CONTINUE
RETURN
END

```

----- THE FOLLOWING SUBROUTINE FINDS OUT STANDERD DEVIATION -----

```

SUBROUTINE STADEV(X,FF,N,M,RSSQ)
DIMENSION X(3),FF(3,3),FFT(3,3),FY(3)
INDIC=-1
DO 10 I=1,N
DO 10 J=1,N
FFT(I,J)=FF(I,J)
CALL MATINV(N,FFT,FY,INDIC,3)
SIGMA1=RSSQ/(FLOAT(M-N))
DO 15 I=1,N
DO 15 J=1,N
IF(I.EQ.J)GOTO 20
GOTO 15
FFT(I,J)=SIGMA1*FFT(I,J)
SD2=FFT(I,J)
SD1=SQRT(ABS(FFT(I,J)))
WRITE(22,302)I,X(I),SD1,RSSQ
WRITE(5,302)I,X(I),SD1,RSSQ
FORMAT(10X,'X(',I1,')=' ,E15.8,3X,'SD1=' ,E15.8,3X,'RSS=' ,E15.8)
CONTINUE
RETURN
END

```

----- SUBROUTINE FOR INVERSION OF MATRIX -----

```

SUBROUTINE MATINV(N,A,X,INDIC,NRC)
DIMENSION IROW(3),JCOL(3),JORD(3),Y(3),A(NRC,NRC),X(3)
EPS=1.0E-15
MAX=N
IF(N.LE.20)GOTO 5
GOTO 75
DETER=1.
DO 18 K=1,N
X(K)=K-1

```

```

PIVOT= 0.0
DO 11 I=1,N
DO 11 J=1,N
IF(K.EQ.1)GOTO 9
DO 8 ISCAN=1,KM1
DO 8 JSCAN=1,KM1
IF(I.EQ.IROW(ISCAN))GOTO 11
IF(J.EQ.JCOL(JSCAN))GOTO 11
CONTINUE
IF(ABS(A(I,J)).LE.ABS(PIVOT))GOTO 11
PIVOT=A(I,J)
IROW(K)=I
JCOL(K)=J
CONTINUE
IF(ABS(PIVOT).GT.EPS)GOTO 13
GOTO 75
IROWK=IROW(K)
JCOLK=JCOL(K)
DETER=DETER*PIVOT
DO 14 J=1,MAX
A(IROWK,J)=A(IROWK,J)/PIVOT
CONTINUE
A(IROWK,JCOLK)=1./PIVOT
DO 18 I=1,N
AIJCK=A(I,JCOLK)
IF(I.EQ.IROWK)GOTO 18
A(I,JCOLK)=-AIJCK/PIVOT
DO 17 J=1,MAX
IF(J.NE.JCOLK)A(I,J)=A(I,J)-AIJCK*A(IROWK,J)
CONTINUE
CONTINUE
DO 20 I=1,N
IROWI=IROW(I)
JCOLI=JCOL(I)
JORD(IROWI)=JCOLI
IF(INDIC.GE.0)X(JCOLI)=A(IROWI,MAX)
CONTINUE
INTCH=0
NM1=N-1
DO 22 I=1,NM1
IP1=I+1
DO 22 J=IP1,N
IF(JORD(J).GE.JORD(I))GOTO 22
JTEMP=JORD(J)
JORD(J)=JORD(I)
JORD(I)=JTEMP
INTCH=INTCH+1
CONTINUE
IF(INTCH/2*2.NE.INTCH) DETER=-DETER
IF(INDIC.LE.0)GOTO 26
GOTO 75
DO 28 J=1,N
DO 27 I=1,N
IROWI=IROW(I)
JCOLI=JCOL(I)
X(JCOLI)=A(IROWI,J)
CONTINUE
DO 28 I=1,N
A(I,J)=Y(I)
CONTINUE

```

```
00 30 I=1,N
00 29 J=1,N
IRDJ=IRDJ(J)
JCOLJ=JCOL(J)
Y(IRDJ)=A(I,JCOLJ)
CONTINUE
00 30 J=1,N
A(I,J)=Y(J)
WRITE(22,301)
00 45 I=1,N
WRITE(22,302)(A(I,J),J=1,N)
FORMAT(/10X,'MATRIX INVERSE IS CALLED'/)
FORMAT(10X,6(4X,E15.8)/)
RETURN
END
```